1

Fuels and Combustion

Syllabus

A) Fuel : - Definition, Characteristics of good fuel.

B) Calorific value (Definition, Types, Determination, Dulong's formula, Numerical)

C) Coal : - Analysis of coal - Proximate analysis, Ultimate analysis, Numerical

D) Combustion of coal - Numerical.

1.1 Introduction

- Fuels are all those substances which on combustion give large amount of heat energy.
- During combustion they combine with oxygen to form various combustion products, and side by side produce a huge amount of heat energy.
- Thus fuel is an essential requirement of industries as well as of domestic operations, to get heat energy required to conduct various processes.

1.1.1 Definition of Fuels

- Fuels can be defined as, "substances which undergo combustion in the presence of air to produce a large amount of heat that can be used economically for domestic and industrial purpose".
- This definition does not include nuclear fuel because it cannot be used easily by a common man.
- The various fuels used economically are wood, coal, kerosene, petrol, diesel gasoline, coal gas, producer gas, water gas, natural gas (LPG) etc.
- The fossil fuels such as wood, vegetable oils etc., which burn to produce heat are called as chemical fuels.

1.1.2 Classification of Chemical Fuels

- Chemical fuels can be broadly classified on the basis of origin as,
  (i) Primary or natural fuels
  (ii) Secondary or artificial or derived fuels.
- On the basis of physical state both the fuels are further classified into :
  (i) Solid fuels
  (ii) Liquid fuels
  (iii) Gaseous fuels
- Primary and secondary fuels can be in any physical state. The following table summarises the fuels in different classes on the basis of their origin and physical state.
- Thus, the Fig. 1.1.1 shows the various fuels categorized on the basis of their origin and/or physical state.

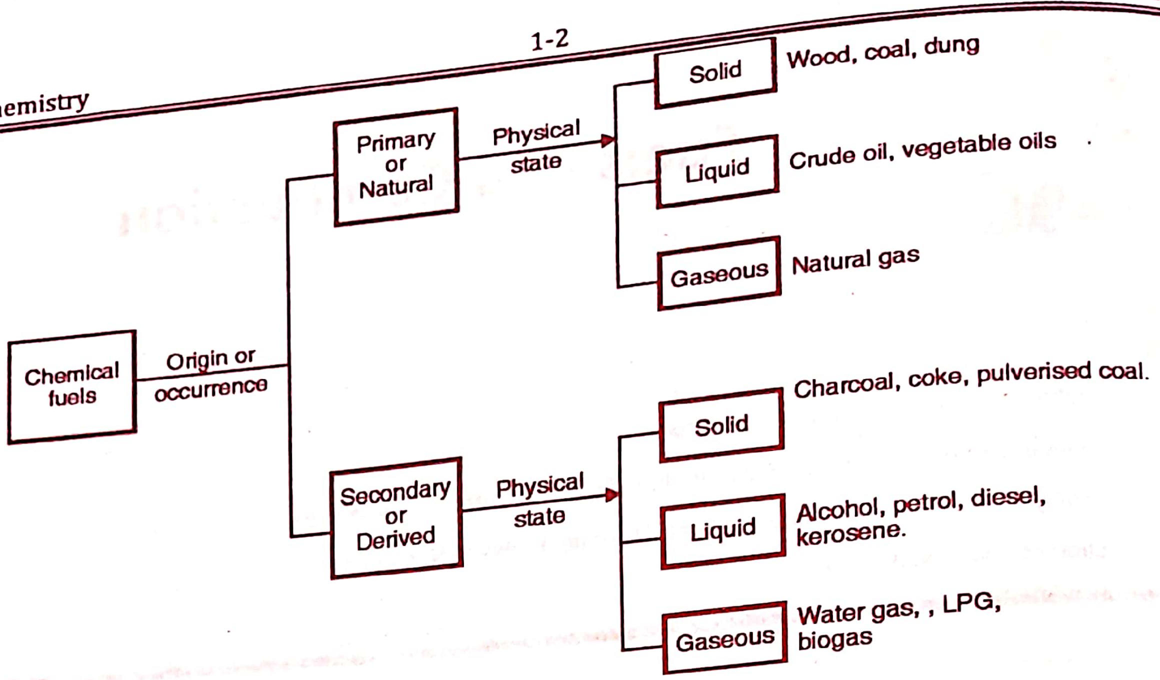


Fig. 1.1.1 : Classification of fuels

1.1.3 Characteristic Properties of Good Fuels

- Fuels are characterized by testing certain physical and chemical properties.
- The physical properties for which fuels are tested and their ideal requirements are listed below. This help i selection of a fuel for given purpose :
  - (i) Calorific value should be as high as possible.
  - (ii) Ignition temperature – Moderate.
  - (iii) Flame temperature should be as high as possible.
  - (iv) Flash and Fire point should be as high as possible.
  - (v) Aniline point should be low.
  - (vi) Cloud and Pour point should be as low as possible.
  - (vii) Viscosity should be adequate.
  - (viii) Coke number should be as high as possible.
  - (ix) Moisture content – As low as possible.
  - (x) Volatile matter – As low as possible.
  - (xi) Ash matter should be absent.
  - (xii) Easy risk free transportation should be possible.
  - (xiii) Storage space – Ideally fuel should occupy small space.
  - (xiv) Air requirements – Adequate.
  - (xv) Harmless products should be produced on combustion.
- The chemical properties include the compositional analysis of fuel. This includes :

For solid and liquids fuels

(i) Percentage of various elements such as C, H, O, N, S, etc.

(ii) Percentage of moisture

(iii) Percentage of volatile matter

For gaseous fuels

(i) Percentage of combustible gases e.g. – CO, H_2, CH_4, C_2H_4, C_2H_6, C_4H_{10}, H_2S etc.

(ii) Percentage of non-combustible gases e.g. N_2, CO_2 etc.

1.2 Calorific Value - G.C.V. and N.C.V.

- Amongst all the above properties, the most important for fuels is calorific value; which can be defined as *"the number of units of heat evolved during complete combustion of unit weight of the fuel".*
- Calorific value can also be defined as, "the number of parts of water which gets heated through 1°C by the heat evolved by the complete combustion of one unit weight of fuel (unit volume for gaseous fuels) under the conditions such as, (i) whole of heat evolved is absorbed by water (ii) the products formed leave the system at atmospheric temperature and pressure".
- From both the above definitions, it is clear that a fuel, to be most useful, must possess high calorific value because the heat evolved by combustion of definite weight of fuel is directly related/proportional to the calorific value of the fuel.

Ignition temperature :

- Ignition Temperature is Minimum temperature to which a substance must be heated before it burns spontaneously independently of the source of heat;

  e.g. ethanol has an ignition temperature of 425°C/798°F and a flash point of 12°C/54°F.
- Each fuel should be brought above its Ignition Temperature for starting the combustion process. An appropriate air-fuel ratio is also necessary. The minimum ignition temperature at atmospheric pressure for some substances are :
  - carbon 400° C
  - gasoline 260° C
  - hydrogen 580° C
  - carbon monoxide 610° C
  - methane 630° C

1.2.1 Units of Calorific Value

- The calorific value of solid fuels is expressed as British Thermal Units per Pound (B.T.U. per 1b) or Kilogram Centigrade Unit per kilogram (K.C.U. per kg.)
- A British Thermal Unit may be defined as, the heat required to raise the temperature of one pound of water from 60° F to 61° F.
- The Calorie, a unit of heat may be defined as, the heat required to raise the temperature of one kg of water from 15°C to 16°C.
- Taking both above definitions of these units, a correlation between them be writes as,

$$1 \text{ B.T.U.} = 2.252 \text{ k.cals} = 252 \text{ cals}$$

$$1 \text{ k.cal} = 1000 \text{ cals}$$

$$1 \text{ k.cal} = 3.968 \text{ B.T.U.}$$

- The calorific value can also be expressed as centigrade heat unit (C.H.U) which is the amount of heat required to raise temperature of 1 pound water through one degree centigrade.

$$\text{Thus } 1 \text{ k.cal} = 2.2 \text{ C.H.U} = 3.968 \text{ B.T.U.}$$

$$\text{Also } 1 \text{ k.cal/kg} = 1.8 \text{ BTU/1b}$$

$$1 \text{ k.cal/m}^3 = 0.1077 \text{ BTU/ft}^3$$

$$1 \text{ BTU/ft}^3 = 9.3 \text{ k.cals/m}^3$$

1.2.2 High and Low Calorific Values

- Calorific values are of two types as,
  (i) High or Gross Calorific Value (H.C.V. or G.C.V.)
  (ii) Low or Net Calorific Value (L.C.V. or N.C.V.)
- High calorific value may be defined as, "the total amount of heat products when one unit of the fuel has been burnt completely and the products combustion have been cooled to 16°C or 60°F".
- Low calorific value may be defined as, "the net heat produced when unit mass or volume of fuel is completely burnt and products are allowed to escape".

Thus,

$$\text{Net or low C.V.} = \text{Gross C.V.} - \text{Latent heat of water formed}$$

$$\text{Or} = \text{Gross C.V} - \text{Mass of hydrogen} \times 9 \times \text{Latent heat of steam}$$

(Because 1 part by weight of hydrogen produces 9 parts (1 + 8) by mass of water)

1.2.3 Dulong Formula

- The calorific value of fuels (e.g. Coal) is determined theoretically by Dulong formula, or I.A. Davies formula.
- Dulong formula can be expressed as,

$$Q = \frac{1}{100}\left[8080\,C + 34500\left(H - \frac{O}{8}\right) + 2240\,S\right]$$

Where,

Q = Calorific value in K.C.U/kg

C = % Carbon

H = % Hydrogen

O = % Oxygen

S = % Sulphur

- In this formula, it is assumed that calorific value of fuel is nothing but the sum total of calorific values of each element and oxygen in fuel (coal) is in combined state as water and hence it does not contribute to heating value of fuel.
- The same formula in terms of H.C.V and L.C.V can be expressed as,

$$\text{H.C.V} = \frac{1}{100}\left[8080\,C + 34500\left(H - \frac{O}{8}\right) + 2240\,S\right]$$

$$\text{and} \quad \text{L.C.V} = \left[\text{H.C.V} - \frac{9}{100} H \times 587\right]$$

- Experimentally the calorific value of solid and liquid fuels is determined by using Bomb calorimeter.

Ex. 1.2.1 : A sample of coal contains, C = 60%; O = 33%; H = 6%; S = 0.5%; N = 0.3%; Ash = 0.2%. Calculate the gross calorific value of the coal.

Soln. :

$$\text{Gross calorific value (or H.C.V)} = \frac{1}{100}\left[8080C + 34500\left(H - \frac{O}{8}\right) + 2240\,S\right]$$

$$= \frac{1}{100}\left[8080 \times 60 + 34500\left(6 - \frac{33}{8}\right) + 2240 \times 0.5\right]$$

$$= 5506 \text{ kcal/kg.}$$

Net calorific value (or L.C.V) $= [\text{H.C.V.} - (0.09 \times \%H \times 587)]$

$= 5506 - (0.09 \times 6 \times 587) = 5506 - 316.98$

$= 5189.02$ kcal/kg

Ans. :

H.C.V = 5506 kcal/kg

L.C.V = 5189.02 kcal/kg

1.3 Solid Fuels

- The solid fuels are available in nature (primary fuels) and also prepared artificially known (secondary fuels).
- The common natural solid fuels are wood, peat, lignite and coal.
- The artificial solid fuels are charcoal, coke, briquettes.
- Other industrial fuels are fossil coals, oil shales, furnace slags, peat, boiler slags, anthracite etc.
- Coal is a combustible solid fuel. By and large, all the solid fuels are formed in nature from cellulose, lignin, proteins, resins, fats and waxes.
- All these raw materials, which are formed under the earth by the burials of partially decomposed vegetation, undergo fermentation liberating CH_4, CO_2 and H_2 gas and form peat, which is slowly converted into lignite and then by further pressure and heat, anthracite is formed.
- Transformation of coal in lignite to anthracite is known as metamorphism or progressive alteration in natural series.

1.3.1 Comparison of Solid, Liquid and Gaseous Fuels

Fuels are classified into three types viz. solids, liquids and gases. Their utility depends upon various factors which are discussed in Table 1.3.1. All fuels have some disadvantages which can be overcome by individual industry.

Table 1.3.1 : Comparison of solid, liquid and gaseous fuels

Sr. No.	Property	Solid Fuels	Liquid Fuels	Gaseous Fuels
1.	Calorific value	Low	Higher	Highest
2.	Specific gravity	Highest	Medium	Lowest
3.	Ignition point	High	Low	Lowest
4.	Efficiency	Poor	Good	Best
5.	Air required for combustion	Large and excess of air	Less excess of air	Slight excess of air
6.	Use in I.C. engine	Cannot be used	Already in use	Can be used
7.	Mode of supply	Cannot be piped	Can be piped	Can be piped
8.	Space for storage	Large	50% less than solid fuel	Very high space
9.	Relative cost	Cheaper	Costly	More costly than other two
10.	Care in storage and transport	Less care required	Care is necessary	Great care required

1.4 Types of Coals

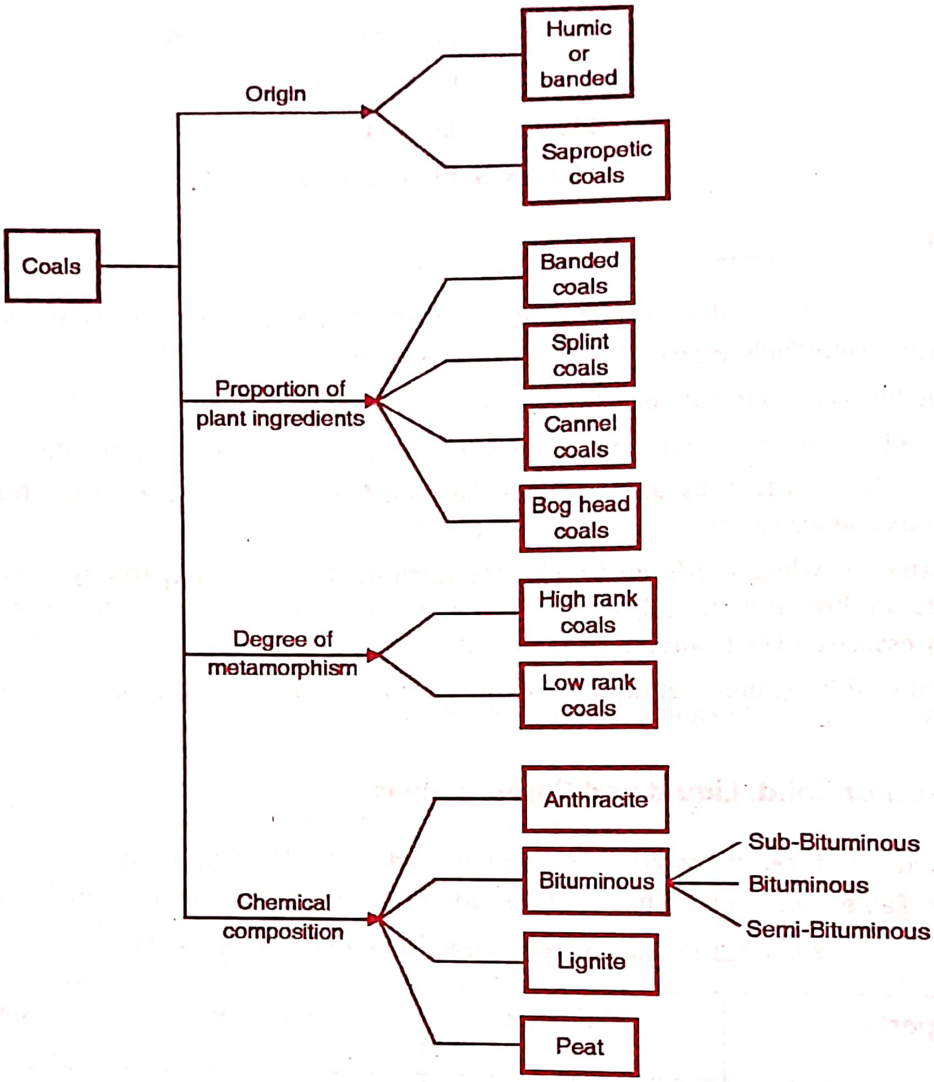


Fig. 1.4.1 : Types of Coals

a) Banded coals

- This type of coal is a variety of bituminous or sub–bituminous coals.
- These are generally formed from peat.
- The structure of this type contains layers or bands of coal forming materials.

b) Splint coals

- This is also a variety of bituminous of sub–bituminous coal, with dull lustre, greyish–black colour.
- The bands of different coal forming materials are more irregular in this variety, as a result it breaks wit irregular rough fracture.
- There is no swelling on burning, but burns freely.

c) Cannel coals

- A variety of bituminous or sub-bituminous coal, with compact fine grained texture instead of bands.
- The colour varies from dark grey to black; possesses high volatile matter, non-coking type, ignites easily and burns with luminous smoky flame.

d) Bog-Head coals

- A variety of bituminous or sub-bituminous coal similar to Cannel coal, in appearance as well as combustibility, but possesses high content of volatile matter and algal remains.
- When subjected to distillation, it gives high yield of tar and oil.

e) High and low rank coals

High rank coals are further sub classified on the basis of their percentage of dry fixed carbon and volatile matter.

Example 1 : Anthracite

There are three types of anthracite (non-coking)

Meta Anthracite	with minimum 92–98% fixed carbon and maximum 2–8% volatile matter.
Anthracite	87-91% fixed carbon, 9-13% volatile matter
Semi-anthracite	86% fixed carbon, 14% volatile matter

Example 2 : Bituminous coals

Low volatile	78% fixed carbon, 22% volatile matter.
Medium volatile	69% fixed carbon, 31% volatile matter.
High volatile	A, B, C, three varieties with less than 69% fixed carbon content with proportionate volatile matter content in respective varieties.

Low rank coals are graded further on the basis of their moist B.T.U., indicating natural moisture.

1.4.1 Coal

- A mined sample of coal contains the coal substance, intermixed with mineral constituents such as kaolin, shale, chloride, sulphides etc. The major constituents of coal are carbon, hydrogen and oxygen. The properties of coal depend upon these constituents.
- There are hundreds of varieties of coal, depending upon its origin and chemical constituents of coal. The important types of coal are peat, lignite, bituminous and anthracite coal. The composition of these major types of coal is given in Table 1.4.1.
- The conversion wood (plant matter) into coal takes place progressively. Depending upon the extent of transformation, coals are divided into 4 types; or grades or ranks.

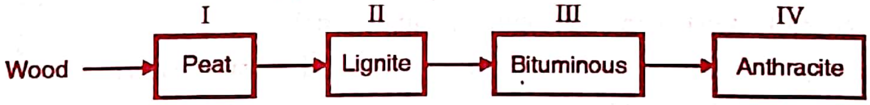


Fig. 1.4.2

During the progressive conversion from peat to anthracite there is;

Increase in	carbon percentage, calorific value, density, lusture, hardness, black colour intensity.
Decrease in	moisture, volatile matter, % of N, H, O, S, ash.

I) Peat

i) Peat is brown and fibrous in texture.

ii) Freshly mined out peat contains large quantity of water as it is found in water logged areas.

iii) Air dried peat contains 15-25% moisture and it crumbles into powder during air drying.

iv) Calorific value of peat is about 5400 cal/gm.

v) It has low density.

vi) It contains 57% C, 6% H, 35% O, 3-6% ash.

Uses

i) Peat type of coal gets powdered during combustion, therefore it is used after briquetting, as domestic and industrial fuel.

ii) It is used for soil conditioning.

iii) On carbonization (heating in absence of air) at 500° C, it produces char oil light spirits.

iv) It can be used for steam raising, thermal insulation, packing, gas purification and sometimes for power generation.

II) Lignite

i) It is the intermediate stage between peat and black coal.

ii) It is brownish black and more compact than peat.

iii) It contains 45-50% volatile matter and burns with long flame.

iv) Its C.V. is 6000-6700 cal/gm and C% = 65-70%.

v) It contains 5% H, 20% O, 10-15% ash.

Uses

i) After briquetting it is used as domestic and industrial fuel.

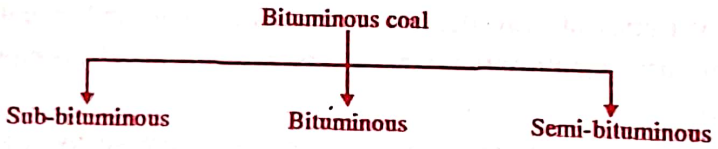
ii) Lignite is used for making 'producer gas'.

iii) It can be used for power generation.

iv) On carbonisation, it gives tar, which is used for making road and recovering various aromatic chemicals.

III) Bituminous Coals

These coals burn with smoky yellow flame and are dark-grey to black. They contain 70-90% C and therefore they are further classified as;



a) Sub-bituminous coal

- This coal has characters between lignite and bituminous coal.
- It is harder and denser than lignite. It is grey black and has dull waxy lusture.
- Its C.V. is about 7000 cal/gm and 70-75% C. It contains large volatile matter 35-40%.
- It crumbles into pieces on air drying and during transportation.
- It is non-caking coal.

Uses :

This coal is used for domestic and industrial purposes.

b) Bituminous coal

- This coal has *banded or laminated* structure with alternate bright and dull layers.
- It has cubical fracture.
- It is black, dense and hard.
- It contains 75-85% C and has C.V. 8000-8500 cal/gm.
- It is a caking coal and forms *coke* and *coal gas* on carbonisation, as it contains 20-30% of volatile matter.

Uses

i) For making metallurgical coke and coal gas as source of various aromatic chemicals.

ii) It is used most widely for domestic and industrial purposes.

iii) It is used for steam generation and power generation.

c) Semibituminous coal

- It has characters between bituminous and anthracite coals.
- It has low volatile matter and caking property.
  (caking = coal decomposing at about 400° C, melting, forming a plastic mass through which V.M. blows out forming highly swollen open structured coal called as coke.)
- Its C.V. is about 8400 cal/gm, C% = 85-90%.

Uses : Making of coke, high temperature heatings, coal gas for tar and chemicals.

IV) Anthracite Coal

This is the highest rank or grade coal.

i) It has C.V. about 8700 cal/gm and 92-98% C.

ii) It contains very low V.M., ash, moisture.

iii) It is highly lustrous black and hard coal.

iv) It shows chonchoidal fracture.

v) It burns with non-smoky short blue flame of high temperature.

Uses

i) Being costly coal, it is used for specific industrial purposes.

ii) It is used as metallurgical fuel.

iii) It is used for making electrodes.

iv) It is used for high temperature heatings.

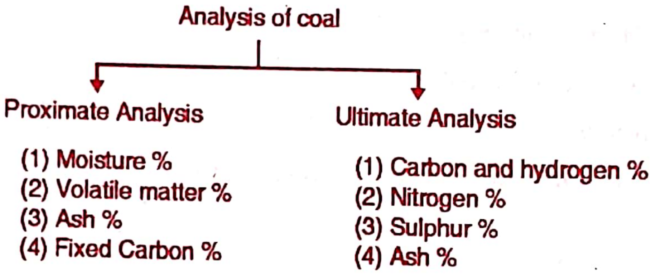
Table 1.4.1 : Types of coals and their chemical composition

Sr. No.	Types of Coal	Moisture of Air Dried At 40°C	C%	H%	O%	Ash%	Calorific Value (kcal/kg)	Uses	Volatile matter %
1.	Peat	15-25%	57	≈ 6	35	3-6	5400	Power generation and domestic purpose.	
2.	Lignite	20	65 to 70	≈ 5	20	10-15	6000 to 6700	Manufacture of producer gas, thermal power plants.	45 to 50
3.	a)Sub Bituminous	Low	70 to 75%	5	15	7	≈ 7000	For metallurgical coke, coal gas, boiler, domestic purpose	35-40%
	b) Bituminous	Low	75 to 85%	5	15	7	8000-8500		20-30%
	c)Semi Bituminous	Low	85 to 90%				≈ 8400		Low
4.	Anthracite	Low	92 to 98%	≈ 3-4	≈ 2-3	Low	8700	Boilers, metallurgical fuel, domestic	Low

The selection of the coal is made by knowing these properties of different types of it given in Table 1.6.2. Thus it becomes easy to select the coal for a particular process. The Table 1.4.1 shows that, as carbon increases from peat to anthracite, the calorific value also increases. The moisture content decreases from peat to lignite. The selection of coal depends on its calorific value, moisture content, ash content and impurities present in it.

1.4.2 Analysis of Coal

- The purposes for coal analysis are :
  i) To decide price of coal.
  ii) To determine quality.
  iii) To specify use of coal for a particular purpose.
  iv) To calculate theoretical calorific value of coal.
  v) To calculate air requirement for complete combustion of coal and design the furnace fire box suitably.
- A sample of coal taken out from coal mine is analyzed in two ways :
  I) Proximate analysis
  II) Ultimate analysis.



- The proximate analysis is easy and quicker and it gives a fair idea of the quality of coal. The ultimate analysis is essential for calculating heat balances in any process for which coal is employed as a fuel.

1.4.2(A) Proximate Analysis of Coal

Proximate analysis is the study or analysis of coal sample in which the following constituents are estimated.

a) Moisture %
b) Volatile matter %
c) Ash %
d) Fixed carbon %

Procedure for proximate Analysis of coal :

a) Moisture %

- A known weight of powdered and air dried coal sample is taken in a crucible (weighed) and it is placed in preheated oven for 1 hour at 110° C. Then the coal is cooled in a desiccator and weighed out.
- If the initial weight of the coal is m gms and final weight is m_1 gms.
- Then the loss in weight $(m - m_1)$ corresponds to moisture in coal.

$$\text{Moisture \%} = \frac{\text{Loss in weight}}{\text{Weight of coal sample}} \times 100 = \frac{(m - m_1)}{m} \times 100$$

b) Volatile matter (V.M.) %

- Moisture free coal left in the crucible in first experiment (m_1) is covered with a lid loosely. Then it is heated at $925^\circ \pm 20^\circ C$ in a muffle furnace for 7 minutes.
- The crucible is taken out and cooled in desiccators. Then it is weighed again, (m_2 gms).

- The loss in weight $(m_1 - m_2)$ is due to loss of volatile matter in the m gms of the coal sample. (Volatile matter is the lower molecular weight organic compounds in coal and they decompose coal during burning of coal and escape without combustion, in the form of smoke).

$$\text{volatile matter \%} = \frac{\text{Weight of volatile matter}}{\text{Weight of air dried coal}} \times 100$$

$$= \frac{(m_1 - m_2)}{m} \times 100$$

- The volatile matter % can also be determined by taking the fresh weight of the air dried coal but the loss in weight at 925° C, will be due to loss of moisture and volatile matter both.
- If w is the weight of air dried coal and w_1 is the mass of coal left at 925° C heating, then

$$\text{Volatile matter \%} = \frac{\text{Loss in weight due to moisture and V.M.} \times 100}{\text{Weigth of coal sample}} - \text{Moisture \%}$$

$$= \frac{(w - w_1) \times 100}{w} - \text{moisture \%}$$

c) Ash %

- The residual coal in the above experiments is heated and burnt in a open crucible at above 750° C for half an hour.
- The coal gets burnt. The ash left in crucible is cooled in a desiccator and weighed $(m_3 g)$.

$$\text{Ash \%} = \frac{\text{weight of ash}}{\text{weight of coal}} \times 100 = \frac{m_3}{m} \times 100$$

d) Fixed carbon %

It is found by calculation, as follows,

$$\text{F.C. \%} = 100 - (\text{moisture \%} + \text{V.M. \%} + \text{ash \%})$$

Significance/ Importance of Proximate Analysis

a) Moisture

i) It decreases calorific value of coal largely as it does not burn and takes away heat in the form of latent heat.

ii) It increases ignition point of coal.

Hence, a coal with lower moisture % is better quality.

b) Volatile matter

i) It decreases calorific value of coal.

ii) It elongates flame and decreases flame temperature.

iii) It forms smoke and pollutes air.

  - The coals containing 15-25% of V.M. on carbonisation gives coke oven gas which is the source of various organic aromatic chemicals.
  - Such coals have good caking property and coke can be obtained from the coals.

iv) The coal with lesser V.M. is better quality coal.

c) Ash

i) Ash reduces calorific value of coal as ash is non-burning part in coal.

ii) Ash disposal is a problem.

iii) Ash fuses to form clinker at high temperature, obstructing the air supply to coal burning in furnace.

Hence, lesser the ash %, better is the quality of coal.

d) Fixed carbon

- Carbon is the burning part in coal and higher the FC% higher is calorific value.
- Hence a good quality coal should have high FC%.

Ex. 1.4.1 : A sample of coal was analysed for content of moisture, volatile matter ash and fixed carbon. From following data, calculate the percentage of the above quantities.

(i) Weight of coal taken = 2.5 gms.

(ii) Weight of coal after heating at 100°C = 2.365 gms.

(iii) Weight of coal after heating covered crucible at 950 ± 20° C = 1.165 gms.

(iv) Constant weight obtained at the end of experiment = 0.460 gms.

Soln. :

Given data : Wight of coal = 2.5 gm = m

Weight of coal after heating at 100°C = 2.365 gm = m_1,

Weight of coal after heating at 950° ± 20°C = 1.165 g = m_3

(a)
$$\text{Moisture \%} = \frac{\text{Loss in weight}}{\text{Weight of coal sample}} \times 100$$
$$= \frac{m - m_1}{m} \times 100$$
$$= \frac{(2.5 - 2.365)}{2.5} \times 100$$
$$= 0.185$$
$$= \frac{0.185}{2.5} \times 100$$
$$= \mathbf{7.4\ \%}$$

(b)
$$\text{Volatile matter (\%)} = \frac{\text{Loss in weight due to volatile matter}}{\text{Weight of coal taken}} \times 100$$
$$= \frac{m_1 - m_3}{m} \times 100$$
$$= \frac{2.365 - 1.165}{2.5} \times 100$$
$$= \frac{1.200}{2.5} \times \frac{100}{1}$$
$$= \mathbf{48\ \%}$$

(c)
$$\text{Ash\%} = \frac{\text{Weight of ash}}{\text{Weight of coal}} \times 100 = \frac{0.460}{2.5} \times 100$$
$$= \mathbf{18.4\%}$$

(d)
$$\text{Fixed carbon \%} = 100 - [\text{\% moisture} + \text{\% V. M} + \text{\% Ash}]$$
$$= 100 - [7.4 + 48.0 + 18.4] = 100 - [73.8]$$
$$= \mathbf{26.2\%}$$

Moisture content = **7.4%,**

Volatile matter content = **48%,**

Ash content = **18.4%.**

Fixed carbon content = **26.2%** ...Ans.

1.4.2(B) Ultimate Analysis of Coal

The analysis of coal in which percentages of C, H, N, S and O (elements) are found out, is known as ultimate analysis.

a) % of C and H in coal

- A known weight of powdered and air dried coal sample is burnt in the presence of pure oxygen, in a combustion apparatus. C and H are converted to CO_2 and H_2O vapours respectively.
- The gaseous products are passed first through the preweighed U-tube containing anhydrous $CaCl_2$ (absorbs H_2O vapours) and then through the KOH solution in a preweighed U-tube (absorbs of CO_2).
- The increase in weight of U-tube containing anhydrous $CaCl_2$ corresponds to weight of water formed and increase in weight of U-tube containing KOH solution corresponds to CO_2 formed, by combusting the coal sample.

$C + O_2 \rightarrow CO_2$; $2\,KOH + CO_2 \rightarrow K_2CO_3 + H_2O$

12 32 44

$H_2 + \frac{1}{2}\,O_2 \rightarrow H_2O$; $CaCl_2 + 7\,H_2O \rightarrow CaCl_2 \cdot 7\,H_2O$

2 16 18

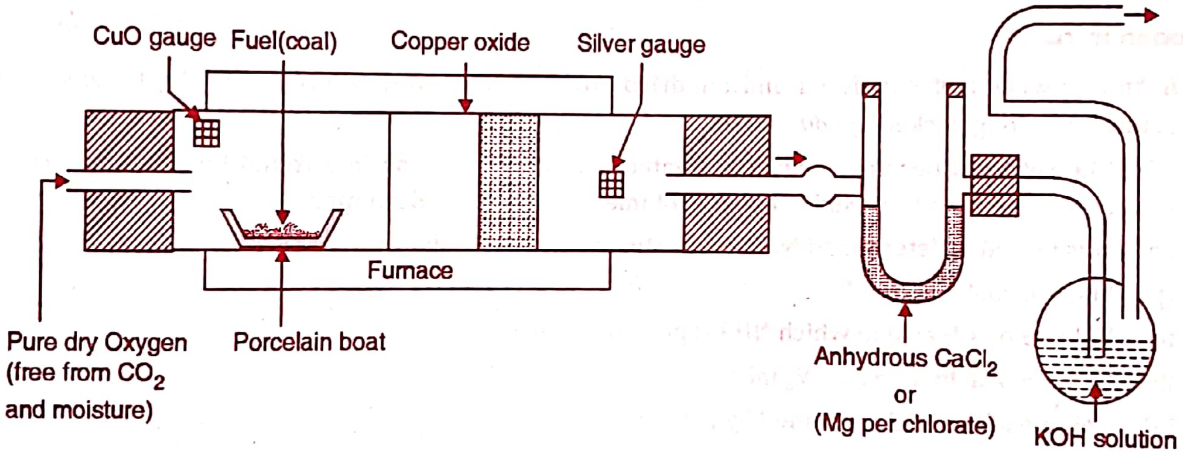

CuO gauge
Fuel(coal)
Copper oxide
Silver gauge
Furnace
Pure dry Oxygen (free from CO2 and moisture)
Porcelain boat
Anhydrous CaCl2 or (Mg per chlorate)
KOH solution

Fig. 1.4.3 : Combustion apparatus

The %C and %H are calculated as follows,

$$C\,\% = \frac{\text{Weight of } CO_2 \text{ formed}}{\text{Weight of coal sample}} \times \frac{12}{44} \times 100$$

$$H\,\% = \frac{\text{Weight of } H_2O \text{ formed}}{\text{Weight of coal sample}} \times \frac{2}{18} \times 100$$

Ex. 1.4.2 : 0.2 gm of coal sample is accurately weighed and is burnt in a combustion apparatus. The gaseous products of combustion are absorbed in potash bulb and calcium chloride tubes of known weight. The increase in weight of potash bulb and $CaCl_2$ tubes are 0.66 gm and 0.08 gm respectively. Calculate the percentage of carbon and hydrogen in the coal sample.

Soln. :

Weight of sample : 0.2 gms

Weight of CO_2 formed : = increase in wt of potash bulb = 0.66 gms

Weight of H_2O formed : = increase in $CaCl_2$ bulb = 0.08 gms

Reactions

$C + O_2 \rightarrow CO_2$ $\qquad$ $2\,KOH + CO_2 \rightarrow K_2\,CO_3 + H_2O$

12 $\quad$ 32 $\quad$ 44

$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$ $\qquad$ $CaCl_2 + 7\,H_2O \rightarrow CaCl_2 \cdot 7\,H_2O$

2 $\quad$ 16 $\quad$ 18

$$\%\ \text{Carbon} = \frac{\text{Weight of } CO_2 \text{ formed}}{\text{Weight of coal sample}} \times \frac{12}{44} \times 100$$

$$= \frac{0.66}{0.2} \times \frac{12}{44} \times 100$$

$$= \mathbf{90\ \%}$$

$$\%\ \text{Hydrogen} = \frac{\text{Weight of } H_2O \text{ formed}}{\text{Weight of coal}} \times \frac{2}{18} \times 100$$

$$= \frac{0.08}{0.2} \times \frac{2}{18} \times 100$$

$$= \mathbf{4.4\ \%}$$

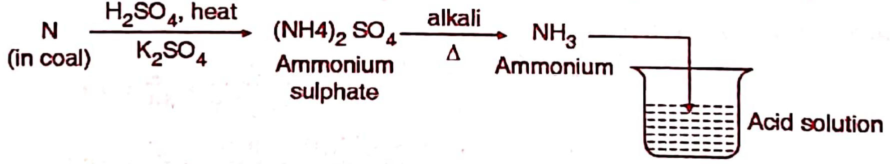
% Carbon = 90 %

% Hydrogen = 4.4 % ...Ans.

b) Nitrogen in coal

- A known weight of powdered and air dried coal is heated with concentrated H_2SO_4 along with K_2SO_4 catalyst in a long necked *Kjeldahl* flask.
- After the contents become clear, it is treated with alkali solution in a round bottom flask. The ammonia (basic gas) liberated is passed in known volume of standard acid solution.
- The unused acid is determined by back titration with NaOH solution.
  - i) Mass of coal = m gm.
  - ii) Volume of × N acid in which NH3 is passed = V_1 ml.
  - iii) Volume of acid unused = V_2 ml
  - iv) Volume of the acid consumed by $NH_3 = (V_1 - V_2)$ m*l*.

$$N\ \% = \frac{\text{Volume of acid consumed} \times \text{normality of acid} \times 1.4}{\text{Weight of coal sample}}$$



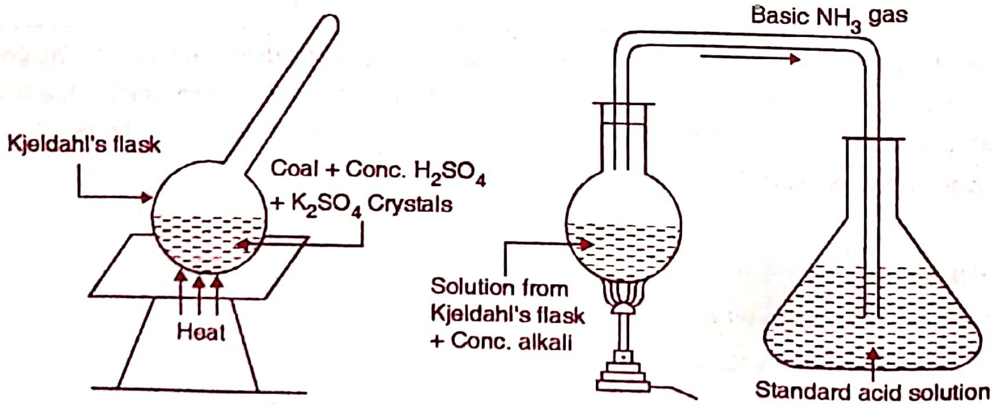


Fig. 1.4.2 : Estimation of nitrogen in coal

c) Sulphur in coal

- Take about 10 *ml* of distilled water in the Bomb pot. Burn the known weight of powdered and air dried coal sample in the Bomb calorimeter experiment.
- Then collect the washings of the Bomb pot in a beaker. Add $BaCl_2$ solution in it.
- Filter the precipitate of $BaSO_4$, dry it and weigh the precipitate of $BaSO_4$. From weight of $BaSO_4$ precipitate, calculate sulphur % as below;

$$S\% = \frac{\text{Weight of } BaSO_4 \text{ ppt}}{\text{Weight of coal sample}} \times \frac{32}{233} \times 100$$

$$\underset{\text{(in coal)}}{S} \xrightarrow{O_2} SO_2 \xrightarrow{O_2} SO_3 \xrightarrow{H_2O} H_2SO_4 \xrightarrow{BaCl_2} 2\,HCl + BaSO_4 \downarrow$$

d) Ash % : As carried out as under proximate analysis. Refer [1.4.2(A)]

e) O % : It is obtained by difference,

$$O\% = 100 - (C\% + H\% + N\% + S\% + ash\%)$$

Significance of Ultimate Analysis

- **Carbon %** : Greater the % of carbon in coal, better is the coal quality and higher calorific value.
- **Hydrogen%** : Most of the hydrogen in coal is in the form of moisture and volatile matter. Only a small percentage of hydrogen is combustible. Thus it decreases C.V. of coal. Smaller the H % better is the coal quality.
- **Nitrogen%** : Nitrogen does not burn during coal combustion and therefore it has no calorific value. Hence a good quality coal should have negligible N%.
- **Sulphur%** : Although sulphur can burn and increase calorific value of coal but it causes SO_x pollution and causes acid rain, corrosion of metallic equipment. Hence, lower the % of S in coal, better is coal quality.
- **Oxygen%** : Most of the oxygen in coal is in the form of moisture. It decreases calorific value of coal (1 % oxygen in coal decreases calorific value by 1.7 %). Hence, lower the O %, better is coal quality.

Ex. 1.4.3 : 3 g of coal was heated in Kjeldahl's flask and NH_3 gas evolved was absorbed in 40 ml of 0.5 N H_2SO_4. After absorption, the excess acid required 18.5 ml of 0.5 N KOH for exact neutralization. 2.3 g of coal sample in quantitative analysis gave 0.35 g $BaSO_4$. Calculate percentage of N and S in coal sample.

Soln. :

Calculation of % nitrogen

Given :

Weight of sample = 3.0 gms

KOH consumed = 18.5 ml

Normality of H_2SO_4 and KOH = 0.5 N

Quantity of H_2SO_4 = 40 ml.

Amount of H_2SO_4 used = (40 – 18.5) ml.

= 21.5 ml.

Equivalents of H_2SO_4 = $21.5 \times 0.5 = 10.75$

= 10.75×10^{-3} milli equivalents

∴ Weight of Nitrogen = $10.75 \times 10^{-3} \times 14 = 0.1505$ gms

$$\therefore \text{ \% Nitrogen} = \frac{\text{Weight of Nitrogen}}{\text{Weight of Coal sample}} \times 100$$

$$= \frac{0.1505}{3} \times 100$$

$$= 5.01 \text{ \%}$$

Percentage of nitrogen in coal sample = 5.01%. ...Ans.

Calculation of % sulphur

Given data :

$$\text{Weight of sample} = 2.3 \text{ gm}$$

$$\text{Weight of } BaSO_4 = 0.35 \text{ gms}$$

$$\text{\% Sulphur} = \frac{\text{Weight of } BaSO_4 \text{ ppt}}{\text{Weight of coal sample}} \times \frac{32}{233} \times 100$$

$$= \frac{0.35}{2.3} \times \frac{32}{233} \times 100$$

$$= \frac{1120}{535.9} = \mathbf{2.09 \text{ \%}}$$

Percentage of sulphur = 0.2 % ...Ans.

1.5 Solved Numericals (G.C.V. , N.C.V. , Calculations by Dulong Formula)

Ex. 1.5.1 : A sample of coal has following composition by mass C = 70%, O = 8%, H = 10%, N = 3%, S = 2%, Ash = 7%. Calculate H.C.V. and L.C.V. using Dulong formula.

Soln. :

$$\text{H.C.V} = \frac{1}{100}\left[8080 \text{ C} + 34500\left(\text{H} - \frac{\text{O}}{8}\right) + 2240 \text{ S}\right]$$

$$= \frac{1}{100}\left[8080 \times 70 + 34500\left(10 - \frac{8}{8}\right) + 2240 \times 2\right]$$

$$= \frac{1}{100}[565600 + 34500\ (10 - 1) + 2240 \times 2]$$

$$= \frac{1}{100}[565600 + 310500 + 4480] = \frac{1}{100}\ [880580]$$

$$= 8805.80 \text{ kcal/kg.}$$

$$\text{L.C.V.} = \left[\text{H.C.V} - \frac{9}{100}\text{H} \times 587\right] \text{kcal/kg.}$$

$$= \left[8805.80 - \frac{9}{100} \times 10 \times 587\right] = [8805.80 - 528.30]$$

$$= 8277.50 \text{ kcal/kg.}$$

H.C.V. = 8805.80 kcal/kg.

L.C.V. = 8277.50 kcal/kg. ...Ans.

Ex. 1.5.2 : A sample of coal contains C = 61%, O = 32%, H = 6%, S = 0.5%, N = 0.2% and Ash = 0.3%. Calculate its G.C.V and N.C.V by Dulong and Petits formula.

Soln. :

$$\text{H.C.V} = \frac{1}{100}\left[8080 \text{ C} + 34500\left(\text{H} - \frac{\text{O}}{8}\right) + 2240 \text{ S}\right]$$

$$= \frac{1}{100}\left[8080 \times 61 + 34500\left(6 - \frac{32}{8}\right) + 2240 \times 0.5\right]$$

$$= \frac{1}{100}[492880 + 34500\,(6-4) + 2240 \times 0.5]$$

$$= \frac{1}{100}[492880 + 69000 + 1120] = \frac{1}{100}[563000]$$

$$= 5630.00 \text{ kcal/kg.}$$

$$\text{L.C.V.} = \left[\text{H.C.V} - \frac{9}{100} H \times 587\right] \text{kcal/kg.}$$

$$= \left[5630.00 - \frac{9}{100} \times 6 \times 587\right] = [5630.00 - 316.98]$$

$$= 5313.02 \text{ kcal/kg.}$$

$$\textbf{H.C.V.} = \textbf{5630.00 kcal/kg}$$

$$\textbf{L.C.V.} = \textbf{5313.02 kcal/kg}$$

...Ans.

Ex. 1.5.3 : A sample of coal contains, C = 70%; O = 20%; H = 8%; S = 0.5%; N = 0.2%; Ash = 1.0%. Calculate the gross and net calorific value of the coal.

Soln. :

$$\text{G.C.V/H.C.V} = \frac{1}{100}\left[8080\text{ C} + 34500\left(\text{H} - \frac{\text{O}}{8}\right) + 2240\text{ S}\right]$$

$$= \frac{1}{100}\left[8080 \times 70 + 34500\left(8 - \frac{20}{8}\right) + 2240 \times 0.5\right]$$

$$= \frac{1}{100}\left[8080 \times 70 + 34500\left(\frac{44}{8}\right) + 2240 \times 0.5\right]$$

$$= \frac{1}{100}[565600 + 189750 + 1120] = 7564.7 \text{ kcal/kg.}$$

$$\text{N.C.V/L.C.V} = [\text{H.C.V.} - 0.09 \times \%\text{H} \times 587]$$

$$= [7564.7 - 0.09 \times 8 \times 587] = 7564.7 - 422.64$$

$$\textbf{N.C.V} = \textbf{7142.06 kcal/kg.}$$

...Ans.

Ex. 1.5.4 : Analysis of a sample of coal gave the following information, C = 80%; H = 6%; O = 8%; S = 2.5%; Ash = 3.5%. Calculate the gross and net calorific value of coal. Also calculate the minimum quantity of air needed for complete combustion of 1 kg. of the above coal.

Soln. :

$$\text{H.C.V.} = \frac{1}{100}\left[8080\text{ C} + 34500\left(\text{H} - \frac{\text{O}}{8}\right) + 2240\text{ S}\right]$$

$$= \frac{1}{100}\left[8080 \times 80 + 34500\left(6 - \frac{8}{8}\right) + 2240 \times 2.5\right]$$

$$= \frac{1}{100}[646400 + 172500 + 5600]$$

$$= 8245 \text{ kcal/kg.}$$

$$\text{L.C.V} = \text{H.C.V.} - (0.09 \times \%\text{ H} \times 587)$$

$$= 8245 - 0.09 \times 6 \times 587 = 8245 - 316.98$$

$$= 7928.02 \text{ kcal/kg.}$$

Quantity of Air Required,

$C + O_2 \rightarrow CO_2$ C = 80 % = 0.80 kg

12 + 32 = 44 H = 6% = 0.06 kg

$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$ O = 8% = 0.08 kg

$2 + 16 = 18$ S = 2.5% = 0.025 kg

$S + O_2 \rightarrow SO_2$

$32 + 32 = 64$

Calculation of oxygen needed for 1 kg coal

Element	%	Weight per kg. of coal	Weight of O_2 in kg.
C	80	0.80	$0.80 \times \frac{32}{12} = 2.133$
H	6	0.06	$0.06 \times \frac{16}{2} = 0.48$
O	8	0.08	–
S	2.5	0.025	$0.025 \times \frac{32}{32} = 0.025$
			Total = 2.638

Weight of oxygen required = Weight of O_2 needed – weight of O_2 present

= 2.638 – 0.08

= 2.558 kg.

Weight of air required for complete combustion [∵ Air contains 23% O_2 by weight]

$= 2.558 \times \frac{100}{23}$ kg

= 11.12 kg.

H.C.V. = 8245 kcal/kg.

L.C.V. = 7928.02 kcal/kg. ...Ans.

Weight of oxygen needed = 2.638 kg.

Weight of air required for complete combustion = 11.12 kg.

Ex. 1.5.5 : A coal is having the following composition by weight, C = 90%; O = 0.3%; S = 0.5%; N = 0.5%; Ash = 2.5%. Net calorific value was found to be 8965.28 k.cal/kg. Calculate the percentage of hydrogen and higher calorific value of coal.

Soln. :

$$\text{N.C.V.} = \text{G.C.V.} - \left[\frac{9}{100} \times \text{H} \times \text{Latent heat}\right]$$

$$\text{N.C.V.} = \frac{1}{100}\left[8080\text{C} + 34500\left(\text{H} - \frac{\text{O}}{8}\right) + 2240\ \text{S}\right] - \frac{9\text{H}}{100} \times \text{Latent heat}$$

Thus,

$$\therefore 8965.28 = \frac{1}{100}\left[(8080 \times 90) + 34500\left(\text{H} - \frac{0.3}{8}\right) + (2240 \times 0.5)\right] - \frac{9}{100} \times \text{H} \times 587$$

solved to find the value of hydrogen.

% of hydrogen = 6.2%

G.C.V. = 9292.83 kcal/kg ...Ans.

Ex. 1.5.6 : A sample of coal contains :

C = 60% O = 33% H = 6%

S = 0.5% N = 0.3% Ash = 0.2%

Calculate the gross and net calorific values.

Soln. :

$$\text{H.C.V.} = \frac{1}{100}\left[8080\text{ C} + 34500\left(\text{H} - \frac{\text{O}}{8}\right) + 2240\text{ S}\right]$$

$$= \frac{1}{100}\left[8080 \times 60 + 34500\left(6 - \frac{33}{8}\right) + 2240 \times 0.5\right]$$

$$= \frac{1}{100}[484800 + 34500\,(6 - 4.13) + 1120]$$

$$= \frac{1}{100}[484800 + 34500\,[1.87] + 1120]$$

$$= \frac{1}{100}[484800 + 64515 + 1120]$$

$$= 5504.35 \text{ kcal/ kg.}$$

$$\text{N.C.V.} = \left[\text{HCV} - \frac{9 \times \text{H}}{100} \times 587\right]$$

$$= \left[5504.35 - \frac{9 \times 6}{100} \times 587\right]$$

$$= [5504.35 - 316.98] = 5187.37 \text{ kcal/kg.}$$

H.C.V. = 5504.35 kcal/kg

N.C.V. = 5187.37 kcal/kg ...**Ans.**

Ex. 1.5.7 : Calculate the gross and net calorific value of coal having following composition : C = 80%, H = 7%, O = 3%, S = 3.5%, N = 2.1% and ash = 4.4%.

Soln. :

$$\text{H.C.V} = \frac{1}{100}\left[8080\text{ C} + 34500\left(\text{H} - \frac{\text{O}}{8}\right) + 2240\text{ S}\right]$$

$$= \frac{1}{100}\left[8080 \times 80 + 34500\left(7 - \frac{3}{8}\right) + 2240 \times 3.5\right]$$

$$= \frac{1}{100}[646400 + 34500\,(7 - 0.38) + 2240 \times 3.5]$$

$$= \frac{1}{100}[646400 + 228390 + 7840]$$

$$= \frac{1}{100}[882630]$$

$$= 8826.30 \text{ kcal/kg.}$$

$$\text{L.C.V.} = \left[\text{H.C.V} - \frac{9}{100}\text{H} \times 587\right]\text{kcal/kg.}$$

$$= \left[8826.30 - \frac{9}{100} \times 7 \times 587\right]$$

$$= [8826.30 - 369.81]$$

$$= 8456.49 \text{ kcal/kg.}$$

H.C.V. = 8826.30 kcal/kg.

L.C.V. = 8456.49 kcal/kg. ...**Ans.**

Ex. 1.5.8 : The % composition of mass of a sample of coal is as follows.

C = 80%, H = 6%, O = 8%, S = 1.5%, N = 1%, ash = rest.

Calculate the gross and net calorific value of Fuels.

Soln. :

$$\text{Gross Calorific Value} = \frac{1}{100}\left[8080\,C + 34500\left(H - \frac{O}{8}\right) + 22405\right]$$

$$= \frac{1}{100}\left[8080 \times 80 + 34500\left(6 - \frac{8}{8}\right) + 2240 \times 1.5\right]$$

$$= 8222.60\ \text{kcal/kg.}$$

$$\text{Net Calorific Value} = [\text{H.C.V.} - (0.09 \times \%\,H \times 587)]$$

$$= [-(0.09 \times 6 \times 587)]$$

$$= 7905.62\ \text{kcal/kg}$$

$$\textbf{H.C.V.} = \mathbf{8222.60\ kcal/kg}$$

$$\textbf{N.C.V} = \mathbf{7905.62\ kcal/kg}$$

...Ans.

Ex. 1.5.9 : Calculate the Gross and Net calorific value of coal sample having the following composition : C – 85%, H – 7%, O – 3%, S – 3.5%, N – 2.1% and Ash – 4.4%.

Soln. :

Given data :

C = 85% S = 3.5%

H = 7% N = 2.1%

O = 3% Ash = 4.4%

To calculate G.C.V. and N.C.V. of coal sample

$$\text{G.C.V.} = \frac{1}{100}\left[8080\,C + 34500\left(H - \frac{O}{8}\right) + 22405\right]$$

$$= \frac{1}{100}\left[8080 \times 85 + 34500\left(7 - \frac{3}{8}\right) + 2240 \times 3.5\right]$$

$$= \frac{1}{100}\,[686800 + 228562.5 + 7840]$$

$$= \frac{1}{100}\,[923202.5] = 9232.025$$

$$\therefore\ \textbf{G.C.V.} = \mathbf{9232.03\ kcal / kg}$$

...Ans.

$$\text{Now N.C.V.} = \text{G.C.V.} - (0.09 \times \%\,H \times 587)$$

$$= 9232.03 - (0.09 \times 7 \times 587)$$

$$= 9232.03 - 369.81$$

$$\textbf{N.C.V.} = \mathbf{8862.22\ kcal / kg}$$

...Ans.

Ex. 1.5.10 : Calculate the gross and net calorific value of coal having following composition.

C = 80%, H = 7%, O = 3%, S = 3.5%, N = 2.1% and ash = 4.4%.

Soln. :

$$\text{G.C.V.} = \frac{1}{100}\left[8080\,C + 34500\left(H - \frac{O}{8}\right) + 2240\,S\right]$$

$$= \frac{1}{100}\left[8080 \times 80 + 34500\left(7 - \frac{3}{8}\right) + 2240 \times 3.5\right]$$

$$= \frac{1}{100}\,[646400 + 226562.5 + 7840] = \frac{1}{100}\,[880802.5]$$

$$\therefore \text{ G.C.V.} = 8808 \text{ Kcals/kg}$$

$$\therefore \text{ N.C.V.} = \text{G.C.V.} - (0.09 \text{ H} \times 587)$$

$$= 8808 - (0.09 \times 7 \times 587) = 8808 - (369.81)$$

$$\therefore \textbf{ N.C.V.} = \mathbf{8438.2 \text{ kcal/kg}}$$

...Ans.

Ex. 1.5.11 : A sample of coal has the following composition by mass.

C = 85%, H = 6%, O = 8%

S = 0.5%, and Ash = 0.5%

Calculate the H.C.V. and L.C.V. using Dulong's formula.

Soln. :

Dulong's Formula :

$$\text{H.C.V} = 1/100 \left(8080 \text{ C} + 34500 \left(\text{H} - \frac{\text{O}}{8}\right) + 2240 \text{ S}\right)$$

$$\text{L.C.V} = \text{H.C.V} - 0.09 \times \text{H} \times 587$$

Numerical solution :

$$\text{H.C.V} = 1/100 \left(8080 \times 35 + 34500 \left(6 - \frac{8}{8}\right) + 2240 \times 0.5\right)$$

$$= 1/100 \,(686800 + 172500 + 1120)$$

$$= 1/100 \,(860420)$$

$$= 8604.2 \text{ K Cal/kg}$$

$$\text{L.C.V} = 8604.2 - 0.09 \times 6 \times 587$$

$$= 8604.2 - 316.98$$

$$= 8287.22 \text{ K Cal/kg}$$

$$\textbf{H.C.V} = \mathbf{8604.2 \text{ K Cal/kg},}$$

$$\textbf{L.C.V} = \mathbf{8287.22 \text{ K Cal/kg}}$$

...Ans.

Ex 1.5.12 : A sample of coal constrains - C = 70%, O = 23%, H = 5%, S = 1.5 %, N = 0.4%, ash = 0.1%. Calculate G.C.V. and N.C.V. of this fuel.

Soln. ;

Given : C = 70 % S = 1.5 % O = 23 %

N = 0.4 % H = 5 % Ash = 0.1 %

To calculate G.C.V. and N.C.V.

$$\text{G.C.V.} = \frac{1}{100}\left[8080 \times \text{C} + 34500 \left(\text{H} - \frac{\text{O}}{8}\right) + 2240 \times \text{S}\right] \text{Kcal/kg}$$

$$= \frac{1}{100}\left[8080 \times 70 + 34500 \left(5 - \frac{23}{8}\right) + 2240 \times 1.5\right] \text{Kcal/kg}$$

$$= \frac{1}{100}\,[565600 + 95625 + 3360] \text{ Kcal/kg}$$

$$\textbf{G.C.V.} = \mathbf{6615.61 \text{ Kcal/kg}}$$

...Ans.

$$\text{N.C.V.} = \text{G.C.V.} - \left[\frac{9\text{H}}{100} \times 587\right] = 6615 - \left[\frac{9 \times 5}{100} \times 587\right]$$

$$= 6615.61 - 264.15$$

$$\textbf{N.C.V.} = \mathbf{6351.46 \text{ Kcal/kg}}$$

...Ans.

1.5.13 : A sample of coal has the following composition - C = 90%, H = 8%, N = 2%, S =1.5%, O = 5% and remaining ash. Calculate the G.C.V. and L.C.V. (Latent heat of condensation of steam = 587 cal/g)

l. :

$$\text{G.C.V.} = \frac{1}{100}\left[8080 \times C + 34500\left(H - \frac{O}{8}\right) + 2240S\right] \text{Kcal/kg}$$

$$= \frac{1}{100}\left[8080 \times 90 + 34500\left(8 - \frac{5}{8}\right) + 2240 \times 1.5\right] \text{Kcal/kg}$$

$$= \frac{1}{100}\left[727200 + 254437.5 + 3360\right] \text{Kcal/kg}$$

$$= \frac{1}{100}\left[984997.5\right] \text{Kcal/kg}$$

$$\therefore \text{G.C.V.} = 9849.975 \text{ K.cal/kg}$$

$$\text{L.C.V.} = \text{G.C.V.} - \left[0.09 \times H \times 587\right] \text{kcal/kg}$$

$$= 9849.975 - \left[0.09 \times 8 \times 587\right] \text{kcal/kg}$$

$$= \left[9849.975 - 422.84\right] \text{kcal/kg}$$

$$\therefore \text{L.C.V.} = 9427.335 \text{ kcal/kg}$$

$$\textbf{G.C.V.} = \mathbf{9849.975 \text{ kcal.kg}}$$

$$\textbf{L.C.V.} = \mathbf{9427.335 \text{ kcal/kg}}$$

...Ans.

1.5.14 : A sample of coal has the following composition by weight :
C = 82%, H = 6%, O = 8%, S = 0.5%, N = 3% and Ash = 0.5%. Calculate the Gross and Net Calorific value using Dulong's formula.

. :

To Calculate Gross and Net calorific value,

Dulong formula,

$$\text{G.C.V} = \frac{1}{100}\left[8080\text{ C} + 34500\left(H - \frac{O}{8}\right)\right] + 2240\text{ S}) \text{ kcal\kg.}$$

$$= \frac{1}{100}\left[8080 \times 82 + 34500\left(6 - \frac{8}{8}\right) + 2240 \times 0.5\right] \text{kcal\kg}$$

$$= \frac{1}{100}\left[662560 + 172500 + 1120\right] \text{kcal/kg}$$

$$= \frac{1}{100}\left[836180\right] = 8361.80 \text{ kcal/kg}$$

$$\textbf{G.C.V} = \mathbf{8361.80 \text{ kcal/kg}}$$

...Ans.

$$\text{Net Calorifc Value} = \text{G.C.V.} - \left[\frac{9 \times H}{100} \times 587\right] \text{kcal\kg.}$$

$$= 8361.80 - \left[\frac{9 \times 6}{100} \times 587\right] \text{kcal/kg}$$

$$= 8361.80 - 316.98$$

$$\textbf{N.C.V} = \mathbf{8044.82 \text{ kcal\kg.}}$$

...Ans.

1.5.15 : A sample of coal has the following composition by mass : C = 80%, H = 4%, O = 6%, S = 3%, N = 2% and Ash = 5%. Calculate gross and net calorific value using Dulong's formula.

Soln. :

$$\text{G.C.V.} = \frac{1}{100}\left[8080\text{ C} + 34500\left(\text{H} - \frac{\text{O}}{8}\right) + 2240\text{ S}\right]$$

$$= \frac{1}{100}\ [8080 \times 80 + 34500\ \left(4 - \frac{6}{8}\right) + 2240 \times 3]$$

$$= \frac{1}{100}\ [646400 + 112125 + 6720] = \frac{1}{100}\ [765245]$$

$$\therefore \text{G.C.V.} = 7625.45\text{ Kcal / Kg}$$

$$\therefore \text{N.C.V.} = \text{G.C.V.} - (0.09\text{ H} \times 587)$$

$$= 7625.45 - (0.09 \times 4 \times 587) = 7625.45 - (211.32)$$

$$\therefore \text{N.C.V.} = 7414.13\text{ Kcal /Kg}$$

G.C.V. = 7625.45 kcal/kg.

N.C.V. = 7414.13 kcal/kg. ...**Ans.**

Ex. 1.5.16 : A sample of coal has the following composition by mass : C = 75%, H = 7%, O = 8%, S = 4%, N = 2% and Ash = 4 %. Calculate Gross Calorific value of the fuel using Dulong's formula.

Soln. :

$$\text{H.C.V} = \frac{1}{100}\left[8080\text{ C} + 34500\left(\text{H} - \frac{\text{O}}{8}\right) + 2240\text{ S}\right]$$

$$= \frac{1}{100}[8080 \times 75 + 34500\{7 - 8/8\} + 2240 \times 4]$$

$$= \frac{1}{100}[606000 + 34500\ \{7 - 1\} + 8960]$$

$$= \frac{1}{100}[606000 + 207000 + 8960]\ = \frac{1}{100}\ [821960]$$

$$= \mathbf{8219.60\ kcal/kg.}$$

$$\text{L.C.V.} = \left[\text{H.C.V} - \frac{9}{100}\text{H} \times 587\right]\text{kcal/kg.}$$

$$= [8219.60 - 0.09 \times 7 \times 587]\ = [8219.60 - 369.81]$$

$$= \mathbf{7849.79\ kcal/kg.}$$

H.C.V. = 8219.60 kcal/kg.

L.C.V. = 7849.79 kcal/kg. ...**Ans.**

1.6 Solved Numericals : Combustion of Coal - Requirement of Weight and Volume of O_2 and Air

Ex. 1.6.1 : Calculate the weight and volume of air required for complete combustion of 5 kg. coal with following compositions, C = 85%; H = 10%; O = 5%.

Soln. :

Combustion reactions :

C	+	O_2	→	CO_2	C = 85% = 0.85 kg
12		32	→	44	H = 10% = 0.10 kg
H_2	+	$\frac{1}{2}\ O_2$	→	H_2O	5% = 0.05 kg
2		16	→	18	

Calculation of O_2 needed for 1 kg coal

Elements = Weight in kg	Weight of O_2 required for complete combustion in kg.
C = 0.85	$0.85 \times \frac{32}{12} = 2.26$ kg.
H = 0.1	$0.1 \times 8 = 0.8$ kg.
O = 0.05	–
	Total oxygen = 3.06 kg.

Weight of oxygen required

= Weight of oxygen needed – weight of oxygen present

= 3.06 – 0.05 = **3.01 kg**

∴ Weight of Air required for complete combustion [∵ Air contains 23% O_2 by weight]

$= 3.01 \times \frac{100}{23} =$ **13.08 kg. per 1 kg. coal.**

∴ Air required for 5 kg. of coal

= 13.08 × 5 = **65.40 kg.**

Volume of Air

∵ 28.94 kg. of air = 22,400 ml volume at NTP

∴ 65.4 kg. of air $= \frac{22400 \times 65.4}{28.94} = 50620.6$ ml. Air

= **50.6206 litres of air**

Weight of air required = 65.4 kg.

Volume of air required = 50.62 litres. ...Ans.

Ex. 1.6.2 : Calculate the weight of air needed for complete combustion of 1 gm of coal containing : C = 72%, H = 10%, O = 9%, N = 3% and remaining being ash.

Soln. :

Combustion reactions

$C + O_2 \rightarrow CO_2$ C = 72% = 0.72 kg

12 32 44 H = 10% = 0.10 kg

$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$ O = 9% = 0.09 kg

2 16 18 N = No combustion reaction

Calculation of O_2 needed in kg for 1 kg coal.

Element	Weight	O_2 required for complete combustion
C	0.72	$0.72 \times \frac{32}{12} = 1.92$ kg
H	0.10	$0.1 \times \frac{16}{2} = 0.8$ kg
O	0.09	–
N	0.03	–
		Total oxygen = 2.72 kg

$$\therefore \text{Weight of oxygen required} = \text{Weight of oxygen needed} - \text{Weight of oxygen present}$$
$$= 2.72 - 0.09$$
$$= \mathbf{2.63\ kg}$$

$$\therefore \text{Weight of air required for complete combustion} = 2.63 \times \frac{100}{23}$$
$$= 11.43 \text{ kg per 1 kg coal}$$

Weight of air required for complete combustion = 11.43 kg **...Ans.**

Ex. 1.6.3 : A sample of coal has the following percentage composition by mass :

C = 70% H = 10% O = 5%

N = 2% S = 3% and remaining ash

Calculate the minimum amount of air needed for complete combustion of 1 kg of coal.

Soln. :

Data given : C = 70 % H = 10 %

O = 5 % N = 2 % S = 3 %

Reaction :

$$\underset{12}{C} + \underset{32}{O_2} \rightarrow \underset{44}{CO_2}$$

$$\underset{2}{H_2} + \underset{16}{\frac{1}{2}O_2} \rightarrow \underset{18}{H_2O}$$

C = 70% = 0.70 kg
H = 10% = 0.10 kg

$$\underset{32}{S} + \underset{32}{O_2} \rightarrow \underset{64}{SO_2}$$

S = 3% = 0.03 kg
O = 5% = 0.05 kg

Calculation of O_2 needed for 1 kg coal.

Element weight in kg	**Weight of O_2 required for complete combustion**
C = 0.70	$0.70 \times \frac{32}{12} = 1.87$
H = 0.10	$0.1 \times \frac{16}{2} = 0.80$
S = 0.03	$0.03 \times \frac{32}{32} = 0.03$
O = 0.05	–
Total O_2	2.7 kg

$\therefore$

$$\text{Weight of } O_2 \text{ required} = \text{Weight of } O_2 \text{ needed} - \text{Weight of } O_2 \text{ present}$$
$$= 2.70 - 0.05$$
$$= \mathbf{2.65\ kg}$$
$$\text{Weight of air} = 2.65 \times \frac{100}{23} \text{ kg}$$
$$= \mathbf{11.52\ kg}$$

Weight of air = 11.52 kg **...Ans.**

Ex. 1.6.4 : Calculate the volume of air containing 25 % oxygen by volume at 27° C and 760 mm pressure which will be required for complete combustion of 3 kg fuel containing, C = 75%; H = 23%; and Ash = 2%.

Soln. : Calculation of O_2 needed for 1 kg coal.

Components	% Composition	Weight of elements per kg. of fuel	Weight of O_2 in kg for 1 kg fuel
Carbon	75	0.75	$\frac{32}{12} \times 0.75 = 2.00$
Hydrogen	23	0.23	$\frac{16}{2} \times 0.23 = 1.84$
Ash	2	-	-
			-
		Total O_2	3.84 kg

$\therefore$ Weight of O_2 required per 3 kg of fuel = 11.5275 kg.

Volume of oxygen at NTP

$$\because 32 \text{ kg. of } O_2 \rightarrow 22.4 \text{ cu.m. of } O_2$$

$$\therefore 11.5275 \text{ kg of } O_2 = \frac{22.4 \times 11.5275}{32}$$

$$= 8.06 \text{ cu.m.}$$

$$\text{Now } \therefore \frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$\frac{760 \times 8.06}{273} = \frac{760 \times V_2}{300}$$

$$V_2 = \frac{1837680}{207480}$$

$$\therefore V_2 = 8.857 \text{ cu.m. } O_2$$

But, air contains 25% O_2 by volume.

$\therefore$ 25 cu.m. of O_2 is present in 100 cu.m. of air.

$\therefore$ 8.857 cu.m. of O_2 is present in $\frac{8.857 \times 100}{25}$ = **35.43 cu.m. of air.**

Volume of air = 35.43 cu.m ...Ans.

Ex. 1.6.5 : A sample of coal requires 20% excess air for complete combustion. Calculate weight of air for 250 gm of the coal, if its composition is,

C = 81%, H = 4%, N = 1.5%, S = 1.2%, O = 3%, ash = 9.3%.

Soln. :

Let us calculate the O_2 required for 1 kg of coal first.

$$\text{Weight of carbon} = \frac{81}{100} \times 1 = 0.81 \text{ kg}$$

$$\text{Weight of hydrogen} = \frac{4}{100} \times 1 = 0.04 \text{ kg}$$

$$\text{Weight of sulphur} = \frac{1.2}{100} \times 1 = 0.012 \text{ kg}$$

$$\text{Weight of oxygen} = \frac{3}{100} \times 1 = 0.03 \text{ kg}$$

Calculation of O_2 needed for 1 kg coal.

Reactions	Weight of O_2 required
$C + O_2 \rightarrow CO_2$ 12 32	$0.81 \times \frac{32}{12} = 2.16$ kg
$2\,H_2 + O_2 \rightarrow 2\,H_2O$ 4 32	$0.04 \times \frac{32}{4} = 0.32$ kg
$S + O_2 \rightarrow SO_2$ 32 32	$0.012 \times \frac{32}{32} = 0.012$ kg
	Total O_2 required = 2.492 kg Less O_2 available = - 0.03
	Net O_2 required = 2.462 kg

$$\text{Weight of air required} = \frac{\text{Weight of } O_2 \times 100}{23} = 10.7 \text{ kg air.}$$

As 20% excess is required for complete combustion, then practically required weight of air

$$= \frac{10.7 \times 120}{100} = 12.845 \text{ kg air.}$$

As 1000 gm of coal requires 12.845 kg air.

$$\therefore \text{ 250 gm of coal requires} = \frac{250}{1000} \times 12.845 = \mathbf{3.211 \text{ kg air.}}$$

...Ans.

Ex. 1.6.6 : A petrol sample contains 14% H and 86% C. Calculate volumes of oxygen and air required for complete combustion of 1 kg of the petrol, at STP conditions.

Soln. :

Given data :

$$\text{Weight of petrol} = 1 \text{ kg, weight of C}$$

$$= \frac{86}{100} \times 1 = 0.86 \text{ kg.}$$

$$\text{Weight of H} = \frac{14}{100} \times 1 = 0.14 \text{ kg,} \quad 0\,\% = 0$$

Calculation of O_2 needed for 1 kg coal

Reactions	Weight of oxygen required
$C + O_2 \rightarrow CO_2$	$\frac{32}{12} \times 0.86 = 2.293$ kg
$2\,H_2 + O_2 \rightarrow 2\,H_2O$	$\frac{32}{4} \times 0.14 = 1.12$ kg
	Total $O_2 = 3.413$ kg

As 32 gm O_2 at STP occupies 22.4 lit.

$$\therefore\ 3.413 \times 1000 \text{ gm } O_2 \text{ at STP will occupy } \frac{3.413 \times 1000 \times 22.4}{32} \text{ lit.}$$

$$= \mathbf{2389.3 \text{ litres oxygen gas.}}$$

$$\text{Volume of air at STP} = \text{Volume of } O_2 \times \frac{100}{21} = \mathbf{11377.8 \text{ litres air.}}$$

Volume of O_2 = **2389.3 liters**

Volume of air = **11377.8 liters**

...Ans.

Ex. 1.6.7 : A sample of coal contains C = 65%, H = 13%, O = 6%, S = 4%, N = 2%, and ash = remaining. Calculate the minimum amount of air needed for complete combustion of 1 kg. of coal.

Soln. :

Given data :

C = 65%, H = 13%, O = 6%

S = 4%, N = 2%

ash = Remaining

wt. of coal = 1 kg

To calculate = minimum amount of air.

Combustion reactions

$C + O_2 \rightarrow CO_2$	C = 65% = 0.65 kg
12 32 44	H = 13% = 0.13 kg
$H_2 + \frac{1}{2} O_2 \rightarrow H_2O$	O = 6% = 0.06 kg
2 16 18	S = 4% = 0.04 kg

Calculation of O_2 need for 1 kg coal

elements	Wt of O_2 required for complete combustion of 1 kg coal
C = 0.65	$0.65 \times \frac{32}{12} = 2.26$ kg
H = 0.13	$0.13 \times 8 = 1.04$ kg
O = 0.06	= 0.06 kg
S = 0.04	$0.04 \times \frac{32}{32} = 0.04$ kg
N = 0.02	–

Total oxygen needed = 3.34 kg.

∴ Weight of oxygen required = weight of oxygen needed – weight of oxygen present

= 3.34 – 0.06

= **3.28 kgs**

∴ Weight of air required for complete combustion = $3.28 \times \frac{100}{23}$

= **14.26 kg for 1 kg coal.**

∴ Volume of air

∵ 28.94 kg of air = 22400 at NTP

∴ 14.26 kg of air = $\left[\frac{22400 \times 14.26}{28.94}\right]$ ml of air

= **11.03 litres of air**

Weight of air required = 14.26 kg

Volume of air required = 11.03 litres

...*Ans.*

Ex. 1.6.8 : A coal sample has the following composition by weight. C = 84 %, H = 6%, S = 1%, O = 8% and remaining ash. Calculate the minimum quantity of air required both by weight and volume for the complete combustion of 2 kg of this fuel. (Mol. Wt. of air = 28.94).

Soln. :

Given Data :

Weight of coal sample = 2 kg

C = 84 %   H = 6 %

S = 1 %   O = 8%

Ash = Remaining

To calculate : Minimum quantity of air by weight and volume.

Calculation of O_2 needed for 1 kg coal

Element	%	Weight per kg of coal	Weight of O_2 in kg
C	84	0.84	$0.84 \times \frac{32}{12} = 2.24$
H	6.0	0.06	$0.06 \times \frac{16}{2} = 0.48$
O	8.0	0.08	–
S	1.0	0.01	0.01*32/32=0.01
		Total O_2	2.73 kg

$\therefore$ Weight of oxygen required = weight of O_2 needed – weight of O_2 present

$= 2.72 - 0.08 = \mathbf{2.64\ kg}$

$\therefore$ Weight of air required = Amount of O_2 needed $\times \frac{100}{23}$

For 1 kg coal $= 2.64 \times \frac{100}{23} = \mathbf{11.48\ kgs}$

$\therefore$ for 2 kgs $= 2 \times 11.48 = 22.96$ kgs

$\therefore$ Volume of air = No. of moles of air × 22.4 litres required for 1 kg coal

$$= \frac{11.48}{28.94} \times 22.4$$

$= \mathbf{8.89\ litres}$

$\therefore$ for 2 kgs $= 2 \times 8.89 = \mathbf{17.78\ litres}$

Weight of air = 22.96 kgs

Volume of air = 17.78 litres **...Ans.**

Ex. 1.6.9 : A sample of coal contains C = 75%, H = 12 %, O = 6%, S = 4%, remaining being other impurities and ash. Calculate the minimum amount of air by volume and weight required for complete combustion of 5 kg. of fuel.

Soln. :

Given : C = 75%, H = 12 %, O = 6%, S = 4%, Weight of fuel = 5 kg

To calculate minimum amount of air for complete combustion - by volume and weight

Calculation of O_2 needed for 1 kg coal

Component Weight in Kg	Combustion reaction	Weight of O_2 required in Kg.
C = 0.75	$C + O_2 \rightarrow CO_2$ 12 32 44	$0.75 \times \frac{32}{12} = 2.00$
H = 0.12	$H_2 + \frac{1}{2} O_2 \rightarrow H_2O$	$0.12 \times \frac{16}{2} = 0.96$
S = 0.04	$S + O_2 \rightarrow SO_2$	$0.04 \times \frac{32}{32} = 0.04$
		Total = 3.00 Kg.
O = 0.06		Total required O_2 = 3.00 − 0.06 = 2.94 Kg.

$\therefore$ O_2 required for 5 Kg fuel $= 2.94 \times 5$

$= $ **14.70 Kg**

Now minimum weight of air required

for 5 Kg of fuel $= 14.70 \times \frac{100}{23}$

$= $ **63.91 Kg**

Volume of air required

If 28.94 Kg of air $\equiv$ 22400 ml. at NTP

Then 63.91 Kg of air $\equiv \left[\frac{63.91 \times 22400}{28.94}\right]$ ml. at NTP

$= $ **49467.31 ml. or 49.47 litres at NTP.** ...Ans.

Ex. 1.6.10 : A coal sample has the following composition by weight C = 85%, H = 5%, S = 2%, O = 5% and Ash = 3%. Calculate the minimum quantity of air required both by weight and volume for the complete combustion of 2 kgs of coal.

Soln. :

Calculation of weight of O_2 needed for 1 kg coal

Reaction	Wt. of O_2 required.
$C + O_2 \rightarrow CO_2$ 12 32	$0.85 \times \frac{32}{12} = 2.67$
$2\,H_2 + O_2 \rightarrow 2\,H_2O$ 4 32	$0.05 \times \frac{32}{4} = 0.40$
$S + O_2 \rightarrow SO_2$ 32 32	$0.02 \times \frac{32}{32} = 0.02$
O_2	= 0.05 kg.
Total O_2 required O_2 present	3.09 kg. 0.05 kg.

$\therefore$ O_2 needed $= 3.04$ kg.

$\therefore$ Weight of air required $= 3.04 \times \frac{100}{23}$

$= 13.217$ kg.

$\therefore$ For 2 kg coal $=$ 26.434 kg of air

Volume of Air

$\because$ 28.94 kg air $=$ 22400 ml. volume at NTP.

$\therefore$ 26.434 kg air $= \frac{22400 \times 26.434}{28.94}$ ml.

$= 20460.92$ ml.

Volume of air required $=$ **20.461 litres of air** ...**Ans.**

Ex. 1.6.11 : Calculate the weight and volume of air needed for complete combustion of 1 kg of coal containing, C = 65%, H = 4%, O = 7 %, N = 3.0%

Moisture = 15% and remaining is Ash.

Molecular weight of air = 28.949

Soln. :

Constituents	% by Weight	Weight of each per kg.
C	65	0.65
H	04	0.04
O	07	0.07
N	03	–
Moisture	15	–

(i) Weight of air required $= \frac{100}{23}(2.67C + 8H + S - O)$ kg

$= \frac{100}{23}(2.67 \times 0.65 + 8 \times 0.04 + 0 - 0.07)$ kg

$= \frac{100}{23}(1.733 + 0.32 - 0.07)$ kg

$= \frac{100}{23}(1.9833)$ kg

$\therefore$ Weight of air required $=$ **8.623 kg**

(ii) Volume of air required :

Molecular weight of air $= 28.949$ g.

$\because$ 28.949 kg of air occupies $= 22.4\ m^3$ of air

$\therefore$ 8.623 kg of air occupies $= \frac{8.623}{28.949} \times 22.4$

$=$ **6.672 m^3 of air**

Weight of air required $=$ **8.632 kg**

Volume of air required $=$ **6.679 kg** ...**Ans.**

Ex. 1.6.12 : Calculate the weight and volume of air required for complete combustion of 1 kg of coal containing ; C = 65%, H = 4%, O = 7%, N = 3%, moisture = 15% and remaining is ash. (molecular weight of air = 28.94g).

Soln. : :

% element	Wt. in kg.	Combustion Reaction	Wt. of O_2 required (kg)
C = 65 %	0.65 Kg.	$C + O_2 \rightarrow CO_2$ 12 32	$0.65 \times \frac{32}{12} = 1.73$
H = 4 %	0.04 Kg.	$H_2 + \frac{1}{2} O_2 \rightarrow H_2O$ 2 16	$0.04 \times \frac{16}{2} = 0.32$
O = 7 %	0.07 Kg.	-	0.07
Moisture 15 %	-	-	-
N = 3 %	0.03 Kg.	No reaction	-
		Total O_2 required	2.05
		O_2 present	– 0.07
		O_2 needed	1.98

$$\therefore \text{Weight of air required} = 1.98 \times \frac{100}{23}$$

$$= \boxed{8.6087 \text{ Kg.}}$$

$\therefore$ Volume of air required =

$$\because \; 28.94 \text{ Kg air} \equiv 22400 \text{ ml Volume at NTP}$$

$$\therefore \; 8.6087 \text{ Kg air} \equiv \left[\frac{22400 \times 8.6087}{28.94}\right] = 6663.27 \text{ ml}$$

$$= \boxed{6.663 \text{ litres.}}$$

Ans. :

Wt. of air needed = 8.6087 Kg.

Volume of air needed = 6.663 litres. ...Ans.

Ex. 1.6.13 : A Coal sample has the following composition by weights : C = 82%, H = 3%, O = 8%, S = 2%, N = 2% and Ash = 3%. Calculate the minimum amount of air required both by weight and volume for complete combustion of 2 kg of coal. (Molecular weight of air = 28.949 gm).

Soln. : :

Calculation of Weight of O_2 needed for 1 Kg of coal

% Constituent	Weight in kg.	Combustion Reaction	Weight of O_2 in kg.
C = 82	0.82	$C + O_2 \rightarrow CO_2$ 12 32	$0.82 \times \frac{32}{12} = 2.187$
H = 3	0.03	$H_2 + \frac{1}{2} O_2 \rightarrow H_2O$ 2 16	$0.03 \times \frac{16}{2} = 0.240$

% Constituent	Weight in kg.	Combustion Reaction	Weight of O_2 in kg.
S = 2	0.02	$S + O_2 \rightarrow SO_2$ 32 32	$0.02 \times \frac{32}{32} = 0.020$
O = 8	0.08	–	0.08
		Total O_2 Required	= 2.447
		Oxygen available	– 0.080
		∴ Oxygen needed	2.367 kg.

$$\therefore \text{Weight of air needed} = 2.367 \times \frac{100}{23} \text{ Kg.}$$

$$= 10.29 \text{ kg.}$$

$$\therefore \text{Weight of air for 2 kg coal} = (10.29 \times 2)$$

$$= \mathbf{20.58\ kg}$$

To calculate volume of air for 2 kg coal,

$$\because 28.949 \text{ kg air} \equiv 22.4 \text{ Litres}$$

$$\therefore 20.58 \text{ kg air} \equiv \left(\frac{22.4 \times 20.58}{28.949}\right) \text{Litres}$$

$$\equiv \mathbf{15.92\ Litres}$$

Weight of air = 20.58 kg

Volume of air = 15.92 L **...Ans.**

Ex. 1.6.14 : A sample of coal was found to contain the following constituents C = 81%, O = 8%, S = 1%, H = 5%, N = 1% and Ash = 4%.Calculate the minimum weight and volume of an required for the complete combustion of 1kg of coal.

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Soln. : Let us calculate the O2 required for 1 kg of coal first.

$$\text{Weight of carbon} = \frac{81}{100} \times 1 = 0.81 \text{ kg}$$

$$\text{Weight of hydrogen} = \frac{5}{100} \times 1 = 0.05 \text{ kg}$$

$$\text{Weight of sulphur} = \frac{1}{100} \times 1 = 0.01 \text{ kg}$$

$$\text{Weight of oxygen} = \frac{8}{100} \times 1 = 0.08 \text{ kg}$$

Calculation of O_2 needed for 1 kg coal.

Reactions	Weight of O2 required
$C + O_2 \rightarrow CO_2$ 12 32	$0.81 \times \frac{32}{12} = 2.16$ kg
$2\,H_2 + O_2 \rightarrow 2\,H_2O$ 4 32	$0.05 \times \frac{32}{4} = 0.40$ kg
$S + O_2 \rightarrow SO_2$ 32 32	$0.01 \times \frac{32}{32} = 0.01$ kg

Reactions	Weight of O2 required
	Total O_2 required = 2.57 kg Less O_2 available = – 0.08
	Net O_2 required = 2.49 kg

$$\text{Weight of air required} = \frac{\text{weight of } O_2 \times 100}{23}$$

$$= \frac{2.49 \times 100}{23} = 10.82 \text{ kg air.}$$

Volume of Air

$\therefore$ 28.94 kg. of air = 22,400 ml volume at NTP

$\therefore$ 10.82 kg. of air $= 22400 \times \frac{10.82}{28.94} = 8374.84$ ml.

Air = 8.375 litres of air

Weight of air required = 10.82 kg.

Volume of air required = 8.375 litres ...Ans.

1.7 Solved Numericals : Proximate and Ultimate Analysis

Ex. 1.7.1 : By Kjeldahl's method 1.5 gm. of a sample of coal was analyzed. The ammonia evolved was absorbed in 50 ml. of 0.1 N H_2SO_4. After absorption the excess H_2SO_4 required 35 ml. of 0.1 N *NaOH* for neutralization. Calculate the percentage nitrogen.

Soln. :

Given :

Weight of sample = 1.5 gms

NaOH consumed = 35 ml

Normality of H_2SO_4 and KOH = 0.1 N

Quantity of H_2SO_4 = 50 ml.

Amount of H_2SO_4 used = (50 – 35) ml.

= 15 ml.

Equivalents of H_2SO_4 $= 15 \times 0.1 = 1.5$

$= 1.5 \times 10^{-3}$ milli equivalents

$\therefore$ Weight of Nitrogen $= 1.5 \times 10^{-3} \times 14 = 0.0021$ gms

$$\therefore \text{ \% Nitrogen} = \frac{\text{Weight of Nitrogen}}{\text{Weight of Coal sample}} \times 100$$

$$= \frac{0.0021}{1.5} \times 100$$

= 1.4 %

Percentage of nitrogen in coal sample = 1.4% ....Ans.

Ex. 1.7.2 : 1.56 gm of the coal was Kjeldahlized and NH_3 gas thus evolved was absorbed in 50.0 ml of 0.1 N H_2SO_4. After absorption the excess (residual) acid required 6.25ml of 0.1 N *NaOH* for exact neutralization. 2.60 gm of the coal sample in a qualitative analysis gave 0.1755 gm of *$BaSO_4$*. Calculate the percentage of N and S in the coal sample.

Soln. :

(a) Calculation of % Nitrogen

Data :

$$\text{Weight of coal} = 1.56 \text{ gm.}$$

$$\text{Volume of } H_2SO_4 = 50 \text{ ml.}$$

$$\text{Volume of NaOH} = 6.25 \text{ ml.}$$

$$\text{Normality of } H_2SO_4 \text{ and NaOH} = 0.1 \text{ N.}$$

$$H_2SO_4 \text{ consumed} = 50 - 6.25 = 43.75 \text{ ml.}$$

$$\text{Equivalents of } H_2SO_4 = 43.75 \times 0.1 = 4.375 \times 10^{-3} \text{ milli equivalent}$$

$$\% \text{ Nitrogen} = N_2 = 4.375 \times 10^{-3} \times 14 \text{ gm.}$$

$$= \frac{\text{wt. of Nitrogen}}{\text{wt.of coal sample}} \times 100$$

$$= \frac{4.375 \times 10^{-3} \times 14}{1.56} \times 100 = \mathbf{3.93\%}$$

(b) Calculation of % sulphur

Data :

$$\text{Weight of coal} = 2.60 \text{ gm}$$

$$\text{Weight of } BaSO_4 \text{ formed} = 0.1755 \text{ gm}$$

$$\% S = \frac{\text{Wt. of } BaSO_4 \text{ formed}}{\text{Wt.of coal sample}} \times \frac{32}{233} \times 100$$

$$= \frac{0.1755}{2.60} \times \frac{32}{233} \times 100 = \frac{561.6}{605.8} = \mathbf{0.93\%}$$

$$\mathbf{\% N = 3.93 \%}$$

$$\mathbf{\% S = 0.93 \%}$$

...**Ans.**

Ex. 1.7.3 : By Kjeldahl's method, 3.5 gms of the coal sample was analysed. The NH_3 gas evolved was absorbed in 50 ml of 0.1 N H_2SO_4. After the absorption, the residual (excess) H_2SO_4 required 15 ml. of 0.1 N NaOH for neutralization. Calculate the percentage of nitrogen in the sample of coal.

Soln. :

Given :

$$\text{Weight of sample} = 3.5 \text{ gms}$$

$$\text{NaOH consumed} = 15 \text{ ml}$$

$$\text{Normality of } H_2SO_4 \text{ and NaOH} = 0.1 \text{ N}$$

$$\text{Quantity of } H_2SO_4 = 50 \text{ ml.}$$

$$\text{Amount of } H_2SO_4 \text{ used} = (50 - 15) \text{ ml.} = 35 \text{ ml.}$$

$$\text{Equivalents of } H_2SO_4 = 35 \times 0.1 = 3.5 = 3.5 \times 10^{-3} \text{ milli equivalents}$$

$$\therefore \text{Weight of Nitrogen} = 3.5 \times 10^{-3} \times 14 = 0.05 \text{ gms}$$

$$\therefore \% \text{ Nitrogen} = \frac{\text{Weight of Nitrogen}}{\text{Weight of Coal sample}} \times 100$$

$$= \frac{3.5 \times 10^{-3} \times 14}{3.5} \times 100$$

$$= \frac{3.5 \times 14}{3.5 \times 1000} \times 100 = \frac{3.5 \times 14}{3.5} = 1.4\%$$

Percentage of nitrogen in coal sample = **1.4%.** ...**Ans.**

Ex. 1.7.4 : 1.5 g of a sample of coal was taken for C and H estimation by combustion method. The increase in weights of tube containing anhydrous $CaCl_2$ and bulb containing KOH was found to be 1.25 g and 4.88 g respectively. Calculate the percentage of C and H.

Soln. :

Given Data :

wt. of coal sample = 1.5 gm

Change of wt. of $CaCl_2$ tube = 1.25 gm

Change of wt. of KOH tube = 4.88 gm

To calculate : % C

% H

Reactions :

$$\underset{12}{C} + \underset{32}{O_2} \rightarrow \underset{44}{CO_2} \quad \text{...(Absorbed on KOH)}$$

$$\underset{4}{2H_2} + \underset{32}{O_2} \rightarrow \underset{36}{2H_2O} \quad \text{...(Absorbed on } CaCl_2\text{)}$$

or 2 16 18

Hence wt. of CO_2 obtained = 4.88 gms.

and wt. of H_2O obtained = 1.25 gms

Thus if 44 gm CO_2 = 12 gm Carbon

$$\therefore \quad 4.88 \text{ gm } CO_2 = \frac{4.88 \times 12}{44}$$

$$= 1.231 \text{ gm Carbon}$$

Thus 1.5 gm sample of coal contain 1.231 gm carbon.

$$\therefore \quad \% \text{ Carbon in coal} = \frac{1.231 \times 100}{1.5}$$

$$= 88.7\ \%$$

Similarly,

If 18 gm H_2O = 2 gm Hydrogen

$$\therefore \quad 1.25 \text{ gm } H_2O = \frac{1.25 \times 2}{18} \text{ gm Hydrogen}$$

$$= 0.139 \text{ gm Hydrogen}$$

Thus 1.5 gm sample of coal contains 0.139 gm H_2.

$$\therefore \quad \% \text{ Hydrogen} = \frac{0.139 \times 100}{1.5} = 9.26\ \%$$

% C in coal = 88.7%

% H in coal = 9.26%

...Ans.

Ex. 1.7.5 : 1.95 g of a coal sample was taken for nitrogen estimation by Kjeldahl method. The ammonia liberated required 9.5 ml of 0.4N H_2SO_4 for neutralization. The same sample of coal weighting 1.5 g in a Bomb calorimeter experiment produced 0.35 g of $BaSO_4$. Calculate percentage of N and S.

Soln. : Given Data :

Weight of coal sample for Nitrogen analsysis = 1.95 gm

Volume of H_2SO_4 = 9.5 gm

Normality of H_2SO_4 = 0.4 N

Weight of coal sample = 1.5 gms in Bomb calorimeter

Weight of $BaSO_4$ = 0.35 gms

To calculate : percentage N

$$N\ \% = \frac{\text{Volume of acid consumed} \times \text{Nacid} \times 1.4}{\text{Weight of coal sample}}$$

$$= \frac{9.5 \times 0.4 \times 1.4}{1.95} = 2.73\ \%$$

$$S\ \% = \frac{\text{Weight of } BaSO_4 \text{ ppt.} \times 32 \times 100}{\text{weight of coal sample} \times 233}$$

$$= \frac{0.35 \times 32 \times 100}{1.5 \times 233} = \frac{1120}{349.5}$$

$$\therefore\ S\ \% = 3.20\ \%$$

$$\mathbf{N\ \% = 2.73\ \%}$$

$$\mathbf{S\ \% = 3.20\ \%}$$

...Ans.

Ex. 1.7.6 : 3g of coal was heated in Kjeldahl's flask and NH_3 gas evolved was absorbed in 40 ml of 0.5 N H_2SO_4. After absorption, the excess acid required 18.5 ml of 0.5 N KOH for exact neutralization. 2.3 g of coal sample in quantitative analysis gave 0.35 g $BaSO_4$. Calculate the % of N and S in the sample.

Soln. :

Percentage of N :

Volume of H_2SO_4 = 40 ml

Normality of H_2SO_4 = 0.5 N

Volume of KOH = 18.5 ml

Normality of KOH = 0.5 N

Weight of coal = 3 g

∴ Volume of H_2SO_4 used = (40 – 18.5) ml.

= 22.5 ml

$$\%\ N = \frac{\text{Volume of } H_2SO_4 \text{ used} \times N_{H_2SO_4} \times 1.4}{\text{Weight of coal sample}}$$

$$= \frac{22.5 \times 0.5 \times 1.4}{3}$$

$$\%\ N = \mathbf{5.25\ \%}$$

$$\%\ S = \frac{\text{Weight of } BaSO_4}{\text{Weight of Coal}} \times \frac{32}{233} \times 100$$

$$\%\ S = \frac{0.35}{2.3} \times \frac{32}{233} \times 100 = \mathbf{2.089\ \%}$$

...Ans.

Ex. 1.7.7 : 2.5 gms of coal sample was taken in Silica Crucible and heated in oven maintained at 110° C for one hour. The weight after heating was 2.368 gms. The same sample was analysed for volatile matter, and weight obtained was 1.75 gms. The sample was further treated to get a fixed weight of 0.95 gms. Calculate percentage of moisture, V.M., ash and F.C. for this sample.

Soln. : Weight of moisture = 2.500 – 2.368 gm

= 0.132 gms.

Weight of volatile matter $= 2.368 - 1.750$

$= 0.618$ gms

Weight of ash $= 0.95$ gms

$\therefore$ % moisture $= \frac{0.132}{2.5} \times 100 = \mathbf{5.28\ \%}$

% Volatile matter $= \frac{0.618}{2.5} \times 100 = \mathbf{24.72\ \%}$

% ash $= \frac{0.95}{2.5} \times 100 = \mathbf{38.00\ \%}$

% Fixed carbon $= 100 - [5.28 + 24.72 + 38.00]$

$= 100 - [68.00]$

$\therefore$ **% Fixed carbon $= 32\ \%$** ...Ans.

Ex. 1.7.8 : By Kjeldahle's method, 2.3 gms of coal sample was anlaysed for nitrogen content. The liberated ammonia was neutralized by 12.5 ml. of 0.5 N H_2SO_4 solution. The same weight of sample gave 0.64 gms of $BaSO_4$ precipitate. Calculate percentage of nitrogen and sulphur in the sample.

Soln. :

Percentage of N :

Method 1 :

Normality of H_2SO_4 $= 0.5$ N

Volume of H_2SO_4 used $= 12.5$ ml.

$\therefore$ M_{eq}. of H_2SO_4 $= (12.5 \times 0.5 \times 10^{-3})$

$= 6.25 \times 10^{-3}\ M_{eq}$.

$\therefore$ Weight of N_2 $= (6.25 \times 10^{-3} \times 14)$ gms

$= (87.5 \times 10^{-3})$ gms

$\therefore$ % N $= \frac{\text{Weight of Nitrogen}}{\text{Weight of coal}} \times 100$

$\therefore$ % N $= \frac{87.5 \times 10^{-3}}{2.3} \times 100 = \mathbf{3.80\ \%}$ ...Ans.

Method 2 :

Volume of H_2SO_4 used $= 12.5\%$

Normality of H_2SO_4 $= 0.5$ N

$\therefore$ % N $= \frac{\text{Volume of } H_2SO_4 \text{ used} \times N_{H_2SO_4} \times 1.4}{\text{Weight of coal sample}}$

$= \frac{12.5 \times 0.5 \times 1.4}{2.3} = \mathbf{3.80\ \%}$

% S $= \frac{\text{Weight of } BaSO_4}{\text{Weight of coal sample}} \times \frac{32}{233} \times 100$

$= \frac{0.64}{2.3} \times \frac{32}{233} \times 100$

$= \frac{20.48}{535.9} \times 100$

$\therefore$ **% S $= 3.82\ \%$** ...Ans.

Ex. 1.7.9 : 3.2 gms of coal in Kjeldahl's experiment evolved NH_3 which was absorbed in 40 ml of 0.5 N H_2SO_4. After absorption, the excess acid required 16 ml of 0.5 N KOH for complete neutralization. 2.5 gms of coal sample in quantitative analysis gave 0.42 gm $BaSO_4$. Calculate the % of N and S in the sample.

Soln. :

Weight of coal sample for N_2 analysis $= 3.2g$

Volume of H_2SO_4 $= (40\text{ ml} - 16) = 24\text{ ml}$

$NH_2SO_4 = 0.5\text{ N}$

Weight of coal sample in Bomb calorimeter = 2.5 g.

Weight of $BaSO_4$ ppt $= 0.42$ g.

To Calculate N%

$$= \frac{\text{Volume of acid consumed} \times N_{acid} \times 1.4}{\text{Wt. of coal sample}}$$

$$= \frac{24 \times 0.5 \times 1.4}{3.2}$$

$$= \mathbf{5.25\ \%}$$ ...Ans.

To Calculate S%

$$= \frac{\text{Weight of BaSO}_4\text{ ppt}}{\text{Weight of Coal Sample}} \times \frac{32}{233} \times 100$$

$$= \frac{0.42}{2.5} \times \frac{32}{233} \times 100$$

$$= \frac{13.44}{582.5} \times 100$$

∴ **S% = 2.31 %** ...Ans.

Ex. 1.7.10 : 2.5 of air dried coal sample was taken in a silica crucible, after heating it in an electric oven at 105° – 110°C for 1 hour, the residue was weighed 2.410g, The residue was heated in a silica crucible covered with vented lid at a temperature 950 ± 20°C for exactly 7 minutes. After cooling the weight of residue was found to be 1.78g. The residue was then ignited at 750°C to a constant weight of 0.246g. Calculate the percentage of fixed carbon in a coal sample.

Soln. :

(1) Weight of coal taken = 2.5 g

Mass of moisture in coal = 2.5 – 2.415

= 0.085 g.

$$\therefore \text{ \% of moisture } = \frac{\text{Loss in weight of coal}}{\text{weight of coal taken}} \times 100 = \frac{0.085 \times 100}{2.5}$$

$$= \mathbf{3.4\ \%}$$

(2) Mass of U. Matter = 2.415 – 1.78 = 0.635 g

$$\text{\% of volume Matter } = \frac{0.635 \times 100}{2.5}$$

$$= \mathbf{25.4\ \%}$$

(3) Mass of residue after ignition = 0.246 g

$$\text{\% of Ash } = \frac{\text{Weight of ash left}}{\text{Weight of coal taken}} \times 100 = \frac{0.246 \times 100}{2.5}$$

$$= \mathbf{9.8\ \%}$$

(4)

$$\text{\% of Fixed Carbon} = 100 - (\text{\% Moisture} + \text{V. M} + \text{Ash})$$

$$= 100 - (3.4 + 25.4 + 9.8)$$

$$= 100 - 38.6 = \mathbf{61.4\ \%},$$

$\therefore$ **% Moisture** = **3.4 %,**

$\therefore$ **% Volatile matter** = **25.4 %**

% Ash = **9.8%**

% Fixed Carbon = **61.4%** ...Ans.

Ex. 1.7.11 : 1kg of coal sample was used for determination of Nitrogen by Kjeldhal's method. The ammonia evolved was passed into 50 ml of 0.1N sulphuric acid. The excess acid required 42 ml of 0.1N NaOH for neutralization. Calculate the percentage of N_2.

Soln. : :

Given data:

Weight of coal = 1 kg, Volume of H_2SO_4 = 50 ml.

Normality of H_2SO_4 = 0.1 N, Volume of NaOH = 4.2 ml.

Normality of NaOH = 0.1 N

To calculate % N in coal sample

$$\text{\% N} = \frac{\text{Volume of acid cosumed} \times \text{Normality of acid} \times 1.4}{\text{Weight of coal sample}}$$

Here, Volume of acid consumed = (50 – 42) ml.

= 8 ml.

$\therefore$ Equivalents of H_2SO_4 = 8×0.1

= 0.8 milli equivalents.

$\therefore$ Weight of N_2 = (0.8×14) gms

= 11.2 gm

$$\therefore \text{\% } N_2 = \frac{\text{Weight of } N_2}{\text{Weight of coal sample}} \times 100$$

$$\therefore \text{\% } N_2 = \frac{11.2}{1000} \times 100 = \mathbf{1.12\%}$$

Volatile matter in coal = **1.12 %** ...Ans.

Ex. 1.7.12 : An air dried sample of coal weighing 2.9 g was taken for volatile matter determination. After losing volatile matter the coal sample weighed 1.96 g. If it contains 4.5% moisture, Find the percentage volatile matter in it.

Soln. : :

Given data :

Weight of coal = 2.9 gm

After losing volatile matter = 1.96 gm

% moisture = 4.5 %

To calculate % volatile matter.

Let us calculate weight of coal after losing moisture,

Let the weight be X gms.

$$\text{\% moisture} = \frac{\text{Loss in weight after heating in oven}}{\text{weight of coal}} \times 100$$

$$\therefore \quad 4.5 = \frac{2.9 - X}{2.9} \times 100$$

$$\therefore \quad \frac{4.5 - 2.9}{100} = 2.9 - X$$

$$\therefore \quad X = 2.9 - 0.1305$$

$$= 2.7695 \text{ gm}$$

Now,

$$\% \text{ Volatile matter} = \frac{\text{Loss in weight due to V.M.}}{\text{Weight of coal}} \times 100$$

$$= \frac{2.7695 - 1.9600}{2.9} \times 100$$

$$= \frac{0.8095}{2.9} \times 100$$

$$= \mathbf{27.91\ \%}$$

$$\textbf{Volatile matter in coal} = \mathbf{27.91\ \%} \qquad \textbf{...Ans.}$$

Ex. 1.7.13 : 2.499 gms of coal sample was taken in silica crucible and heated in oven maintained at 110°C for one hour. The weight after heating was 2.368 gms. The same sample was analysed for volatile matter and weight obtained was 1.75g, the sample as further treated to get fixed weight of 0.95 gms. Calculate the percentage of moisture, volatile matter, ash and fixed carbon for this sample.

Soln. :

Given data :

Weight of coal Sample : 2.499 gms. = w_1

Weight of coal after heating at 110°C : 2.388 gms. = w_2

Weight of coal after heating for V.M. : 1.75 gms. = w_3

Fixed weight obtained = 0.95 gms. = w_4

$$\text{To calculate \% moisture} = \frac{\text{Loss in Weight}}{\text{Weight of coal}} \times 100$$

$$= \frac{w_1 - w_2}{w_1} \times 100$$

$$= \frac{0.111}{2.499} \times 100 = 4.44\ \%$$

$$\text{To calculate \% V.M.} = \frac{\text{Loss in weight due to V.M.}}{\text{Weight of coal}} \times 100$$

$$= \frac{w_2 - w_3}{w_1} \times 100$$

$$= \frac{2.388 - 1.75}{2.499} \times 100 = \mathbf{25.53\ \%}$$

$$\% \text{ Ash} = \frac{\text{Constant weight}}{\text{Weight of coal}} \times 100$$

$$= \frac{0.95}{2.499} \times 100 = \mathbf{38\ \%}$$

$$\% \text{ Fixed carbon} = 100 - [\% \text{ moisture} + \% \text{ V.M.} + \% \text{ Ash}]$$

$$= 100 - [4.44 + 25.53 + 38]$$

$$= 100 - [68.97]$$

∴ % Fixed carbon = 31.03 %

∴ % Moisture = 4.44 %,

∴ % Volatile matter = 25.53 %,

% Ash = 38.00 %,

% Fixed Carbon = 31.03 % ...Ans.

Ex. 1.7.14 : A coal sample was subjected to ultimate analysis, 0.6 gm of coal on combustion in a Bomb colorimeter, produces 0.05 gm $BaSO_4$. Calculate the percentage of 'S' in coal sample.

Soln. : :

Weight of coal sample = 0.6 gms.

Weight of $BaSO_4$ = 0.05 gms.

To calculate % S

$$\% S = \frac{\text{Weight of BaSo}_4\text{ ppt}}{\text{Weight of Coal Sample}} \times \frac{32}{233} \times 100$$

$$= \frac{0.05}{0.6} \times \frac{32}{233} \times 100$$

$$= \frac{1.6}{139.8} \times 100 = 1.14\ \%$$

∴ % S = 1.14 % ...Ans.

Ex. 1.7.15 : A coal sample was subjected to ultimate analysis. 1.5g of coal on combustion in a Bomb calorimeter gave 0.42g of $BaSO_4$. Calculate percentage sulphur in the coal sample.

Soln. : :

Weight of Coal Sample = 1.5 gms.

Weight of $BaSO_4$ ppt = 0.42 gms.

To calculate % S in coal sample,

$$\% S = \frac{\text{Weight of BaSO}_4\text{ ppt}}{\text{Weight of coal sample}} \times \frac{32}{233} \times 100$$

$$= \frac{0.42}{1.5} \times \frac{32}{233} \times 100$$

$$= \frac{13.44}{349.5} \times 100 = 3.85\ \%$$

∴ % S = 3.85 % ...Ans.

Ex. 1.7.16 : A coal sample was subjected to ultimate analysis 1.5g of coal on combustion in a Bomb calorimeter gave 0.24g of $BaSO_4$. Calculate percentage sulphur in the coal sample.

Soln. : :

$$\% S = \frac{\text{Weight of BaSO}_4}{\text{Weight of coal sample}} \times \frac{32}{233} \times 100$$

$$= [0.24 \div 1.5] \times \frac{32}{233} \times 100$$

$$= [7.68 \div 349.5] \times 100$$

$$= 2.197\ \% \sim 2.2\ \%$$

∴ % S = 2.197 % ~ 2.2 % ...Ans.

Ex. 1.7.17 : 2.5 g. of a coal sample was analysed for nitrogen content by Kjeldahl's method. The liberated ammonia required 12.7 ml of 0.5N H_2SO_4 solution for neutralization. In a separate experiment, using Bomb calorimeter, 1.5 g of coal sample gave 0.28g of $BaSO_4$. Calculate percentage Nitrogen and Sulphur in the sample.

Soln. : :

Given Data :

Weight of coal sample for Nitrogen analysis = 2.5 gm
Volume of H_2SO_4 = 12.7 ml
Normality of H_2SO_4 = 0.5 N
Weight of coal sample = 1.5 gms in Bomb calorimeter
Weight of $BaSO_4$ = 0.28 gms

To calculate : Percentage N

$$N\% = \frac{\text{Volume of acid consumed} \times \text{N acid} \times 1.4}{\text{Weight of coal sample}}$$

$$= [12.7 \times 0.5 \times 1.4 \div 2.5] = 3.56\,\%$$

$$S\% = \frac{\text{Weight of BaSO}_4\text{ ppt.} \times 32 \times 100}{\text{weight of coal sample} \times 233}$$

$$= \frac{0.35 \times 32 \times 100}{1.5 \times 233} [0.28 \times 32 \times 100] \div [1.5 \times 233]$$

$$= \frac{1120}{349.5} [896 \div 349.5]$$

$$\therefore \quad S\% = 2.56\,\%$$

$$\mathbf{N\ \% = 3.56\,\%}$$

$$\mathbf{S\ \% = 2.56\,\%}$$

...Ans.

Ex. 1.7.18 : A coal sample was subjected to ultimate analysis : 1.6 gm of coal on combustion in a Bomb calorimeter gave 0.47 gm of $BaSO_4$ Calculate % of sulphur in the coal sample. **May 15, 3 Marks**

Soln. : Given data : Weight of $BaSO_4$ ppt : 0.47 gms

Weight of coal sample : 1.6 gms

$$\%S = \frac{\text{Weight of BaSO}_4}{\text{Weight of Coal}} \times \frac{32}{233} \times 100$$

$$= [0.47 / 1.6] \times [32 / 233] \times 100$$

$$\%S = 4.04\ \%$$

***Percentage of sulphur* = 4.04 %** **...Ans.**

Ex. 1.17.19 : 0.5 gm of coal sample was burnt in Bomb. Calorimeter experiment produced 0.06 gm of $BaSO_4$. Calculate percentage of sulphur.

Soln. :

Weight of coal sample = 0.5gms.
Weight of $BaSO_4$ = 0.06gms.

To calculate % S

$$\%S = \frac{\text{Weight of BaSo}_4\text{ ppt}}{\text{Weight of Coal Sample}} \times \frac{32}{233} \times 100$$

$$= 0.06/0.5 \times \frac{32}{233} \times 100$$

$$= 1.92 / 116.5 \times 100$$

$$\therefore \quad \%\ S = 1.65\ \%$$

...Ans.

Ex. 1.17.20 : 1.5 g of a coal sample was burnt in a combustion apparatus and the products of Combustion were collected in previously weighted KOH bulb and C_aCl_2 tube. The increase in Weights of KOH bulb and C_aCl_2 tube were found to be 3.92g and 1.25 g respectively. Calculate percentage carbon and hydrogen in the sample.

May 15, May 16, May 18, 4 Marks

Soln. :

Weight of coal sample = 1.5 gm

Change of wt. of $CaCl_2$ tube = 1.25 gm

Change of wt. of KOH tube = 3.92 gm

To calculate : % C, % H

Reactions :

$C + O_2 \rightarrow CO_2$ ...(Absorbed on KOH)

12 32 44

$2H_2 + O_2 \rightarrow 2H_2O$...(Absorbed on $CaCl_2$)

4 32 36

or 2 16 18

Hence Weight of CO_2 obtained = 3.92 gms.

and Weight of H_2O obtained = 1.25 gms

Thus if 44 gm CO_2 ≡ 12 gm Carbon

∴ 3.92 gm CO_2 ≡ 3.92 * 12/44

= 1.07 gm Carbon

Thus 1.5 gm sample of coal contain 1.231 gm carbon.

∴ % Carbon in coal = 1.07 * 100/1.5 = 71.3 %

Similarly,

If 18 gm H_2O ≡ 2 gm Hydrogen

$$\therefore \quad 1.25 \text{ gm } H_2O \equiv \frac{1.25 \times 2}{18} \text{ gm Hydrogen}$$

≡ 0.139 gm Hydrogen

Thus 1.5 gm sample of coal contains 0.139 gm H_2.

$$\therefore \quad \% \text{ Hydrogen} = \frac{0.139 \times 100}{1.5}$$

$$= \boxed{9.26\ \%}$$

% C in coal = 71.3 % ...**Ans.**

% H in coal = 9.26% ...**Ans.**

Important Terms and Definitions

- Fuels are all those substances which on combustion give large amount of heat energy.
- Fuels can also be defined as substances which undergo combustion in the presence of air to produce a large amount of heat that can be used economically for domestic and industrial purpose.
- This definition does not include nuclear fuel because it cannot be used easily by a common man.
- Calorific value : number of units of heat evolved during complete combustion of unit weight of the fuel.

- Calorific value can also be defined as, the number of parts of water which gets heated through 1°C by the heat evolved by the complete combustion of one unit weight of fuel (unit volume for gaseous fuels) under the conditions such as, (i) whole of heat evolved is absorbed by water (ii) the products formed leave the system at atmospheric temperature and pressure.
- A British Thermal Unit may be defined as, the heat required to raise the temperature of one pound of water from 60° F to 61° F.
- The Calorie, a unit of heat may be defined as, the heat required to raise the temperature of one kg of water from 15°C to 16°C.
- High calorific value may be defined as, the total amount of heat products when one unit of the fuel has been burnt completely and the products combustion have been cooled to 16°C or 60°F.
- Low calorific value may be defined as, the net heat produced when unit mass or volume of fuel is completely burnt and products are allowed to escape.
- The calorific value of fuels (e.g. Coal) is determined theoretically by Dulong formula, or I.A. Davies formula.
- Dulong formula can be expressed as,

$$Q = \frac{1}{100}\left[8080\ C + 34500\left(H - \frac{O}{8}\right) + 2240\ S\right]$$

Where,
Q = Calorific value in K.C.U/kg
C = % Carbon
H = % Hydrogen
O = % Oxygen
S = % Sulphur

The same formula in terms of H.C.V and L.C.V can be expressed as,

$$\text{H.C.V} = \frac{1}{100}\left[8080\ C + 34500\left(H - \frac{O}{8}\right) + 2240\ S\right]$$

and

$$\text{L.C.V} = \left[\text{H.C.V} - \frac{9}{100} H \times 587\right]$$

- Experimentally the calorific value of solid and liquid fuels is determined by using Bomb calorimeter.
- Proximate analysis is the study or analysis of coal sample in which

a) moisture % b) volatile matter %
c) ash % and d) fixed carbon % are determined.

- The analysis of coal in which percentages of C, H, N, S and O elements are found out, is known as ultimate analysis.

$$C\,\% = \frac{\text{Weight of } CO_2 \text{ formed} \times 12 \times 100}{\text{Weight of coal sample} \times 44}$$

$$H\,\% = \frac{\text{Weight of } H_2O \text{ formed} \times 2 \times 100}{\text{Weight of coal sample} \times 18}$$

$$N\,\% = \frac{\text{Volume of acid consumed} \times \text{normality of acid} \times 1.4}{\text{Weight of coal sample}}$$

OR $$N\,\% = \frac{\text{Volume of acid} \times \text{change in normality of acid} \times 1.4}{\text{Weight of coal sample}}$$

$$S\,\% = \frac{\text{Weight of } BaSO_4 \text{ ppt.} \times 32 \times 100}{\text{Weight of coal sample} \times 233}$$

O % : It is obtained by difference,

$$O\,\% = 100 - (C\%\ H\% + N\% + \text{ash}\% + S\%)$$

Unsolved Problems

Prob. 1 : Determine the gross and net calorific value of the fuel which on ultimate analysis gave following results. C = 92%; H = 4%; O = 2%; N = 1%; S = 0.3%; Ash = 0.7%. Assume latent heat of condensation of steam as 580 kcal/kg.

(Ans. : G.C.V. = 8734.07 kcal/kg, N.C.V. = 8525.27 kcal/kg)

Prob. 2 : A sample coal contains C = 76%; O = 16%; H = 5%; N = 1.5%; S = 0.3%; Ash = 1.0%. Calculate the higher and lower calorific value of coal. **(Ans. : G.C.V. = 7182.52 kcal/kg, N.C.V. = 6918.37 kcal/kg)**

Prob. 3 : A sample of coal has following composition by mass C = 75%; H = 6%; O = 8%; Ash = 7.0%.and nitrogen to make 100%. Calculate H.C.V. and L.C.V.. Given that H.C.V. of C = 8080 kcal/kg. H = 34500 kcal/kg and S = 2240 kcal/kg. **(Ans. : H.C.V. = 7785.00 kcal/kg, L.C.V. = 7468.02 kcal/kg)**

Prob. 4 : Calculate weight of the air needed for complete combustion of 5 kg of coal having C = 86%, H = 5%, S = 2.5%, N = 1.5%, remaining ash. **(Ans. : 59.02 kg.)**

Prob. 5 : The percentage analysis of coal contains 85% carbon, 5% hydrogen, 1% suphur, 1% oxygen and remaining ash. Calculate weight and volume of air required for complete combustion of 4 kg of coal.

(Ans. : 46.44 kg and 35.95 cu.m.)

Prob. 6 : The percentage composition of coal sample was C = 84%, H = 6.5%, O = 5.5%, N = 1%, S = 2.0%. Calculate the quantity of oxygen on volume basis required at 27° C and one atmosphere pressure for combustion of 1.5 kg of coal. **(Ans. : 3.47 cu.m.)**

Prob. 7 : A gas used in internal combustion engine has 45% H_2,35% CH_4, 15% CO and 5% N_2. Find the volume of air needed for the complete combustion of one cu.m. of gas. **(Ans. : 4.76 cu.m.)**

Review Questions

Q. 1 Define fuels. How are they classified ?

Q. 2 Distinguish between Proximate analysis and ultimate analysis.

Q. 3 How is proximate analysis of coal conducted? What is its significance?

Q. 4 How is ultimate analysis carried out? What is its significance?

Q. 5 Define Gross and Net calorific value of a fuel.

Q. 6 Differentiate between Gross and Net calorific value of a fuel.

□□□

2

Corrosion

Syllabus

A) Introduction: - Definition, Types of Corrosion – i) Dry or Atmospheric Corrosion, ii) Wet or Electrochemical corrosion (In Acidic medium, In Neutral medium)

B) Factors affecting rate of corrosion:- i) Position of metal in galvanic series, ii) Purity of Metal, iii) Nature of Corrosion product, iv) Temperature, v) pH of medium, vi) concentration of medium, vii) moisture, viii) Relative Cathodic and Anodic area, ix) overvoltage

C) Methods to control corrosion : i) Selection of metal, ii) Proper Designing, iii) Cathodic protection, iv) Use of Corrosion Inhibitors, v) Metallic Coating

D) Corrosion in Electronic devices.

2.1 Introduction

- Corrosion is nothing but the *deterioration* of a substance due to its reaction with its environment. Thus it is the *destruction* of the metal due to *unwanted reaction* between the metal (starting from surface) and the atmosphere. The *tendency* of the metals to undergo such reactions readily with atmospheric gases and other matters, *owes to their origin.*
- Metals occur in nature in the form of their *ores*. These ores are subjected to several metallurgical processes to extract the *metal in pure form*. Thus the extraction processes reduce ores to their *metallic states*. But as soon as the metals are extracted from ores, the metals become *highly reactive* and enter into reaction with the other elements present in the *surrounding/vicinity* of it. This natural reactivity/tendency of metals gives *rise to corrosion*, and thereby metals *again enter into combined states.*
- *Metals show great affinity to oxygen* present in the atmosphere, and form oxides. There are few other impurities of atmosphere which also affect metals, forming *carbonates, sulphides, sulphates* etc. Thus the corrosion can also be defined as, the process by which the metals have a tendency to go back to their combined state is known as *corrosion.*
- The environment/atmosphere surrounding metals can be *air, water, sea water, acids, alkalies, steam, gases, other molten metals, soils,* etc. The metals come in contact with all these *corrosion influencing factors* at varying temperatures ranging from room temperature to working temperature of the various processes. This contact results in gradual transformation of metal into its compounds. This is also known as *weathering of metals or weeping of metals.* Such weathering is exhibited by *timber, wood, concrete etc. Even leading of glass or cracking of plastics are examples of 'corrosion'.*

2.1.1 Corrosion

Q. Define corrosion of metals. **May 16, Dec. 17, May 19, 6 Marks**

"Any process causing deterioration or destruction of any material is known as *corrosion*". *Metals* being *highly reactive*, are greatly affected by action of the factors responsible for corrosion.

Different metals possess affinity for different gases in atmosphere.

For example

1. Iron reacts with oxygen to form oxide.
2. Copper forms *carbonate* by reacting with *CO_2 present in air*
3. *Silver reacts* with *chlorine* or *H_2S* from atmosphere forming corresponding compounds.

Effects of corrosion

(i) Metal loses its efficiency and many of its useful properties get altered.

(ii) Maintenance cost and cost of material increases while production rate decreases.

(iii) The purity of the product gets affected.

Knowing these destructive effects of corrosion, it becomes essential to understand the mechanism of corrosion, which is discussed in this chapter.

2.2 Types of Corrosion

There are two types of corrosion,

	Types of corrosion
(a)	Dry or Atmospheric corrosion / Chemical corrosion
(b)	Wet or Immersed corrosion / Electrochemical corrosion

2.2.1 Dry / Chemical Corrosion/Atmospheric Corrosion

Q. Explain with example how nature of oxidised product affects the rate of corrosion. **May 15, 4 Marks**

Q. What is 'Oxidation corrosion' ? Why do gold and platinum metal not get corroded in atmospheric oxygen ? **Dec. 15, 3 Marks**

Q. Explain how rate of corrosion of the following metals is influenced by atmospheric oxygen. (i) Molybdenum (ii) Tin. **May 16, 3 Marks**

Q. Gold does not get corroded due to oxidation. Why ? **May 17, 3 Marks**

Q. "The noble metals do not undergo corrosion". Justify the statement. **May 19, 3 Marks**

- Chemical/Atmospheric or dry corrosion occurs mainly by, *direct attack* of atmospheric gases such as *O_2, CO_2, H_2S, halogens, SO_2* etc. on the surface of metals. The metal forms corresponding compounds such as *oxides, carbonates, sulphides, halides or sulphates.* The action of some *organic* or *anhydrous inorganic liquids, or melt of metals* also cause this type of corrosion.
- This type of corrosion is divided into following classes :
  (i) Corrosion due to oxygen – leading to formation of oxides.
  (ii) Corrosion due to other gases – leading to formation of other compounds.
  (iii) Corrosion due to other corrosive liquids – such as other molten metal's.

(i) Corrosion due to oxygen

- This type of corrosion occurs due to attack of atmospheric oxygen on metal surface either at low or high temperatures, forming metal oxide as

$$\text{Metal} + O_2 \rightarrow \text{Metal oxide}$$

- Normally, more active metals get corroded faster than less active metals. For example, alkali metals and alkaline earth metals get oxidized even at low temperatures as compared to other metals which are less active.

Mechanism of chemical corrosion due to oxidation

$$\text{Metal} \xrightarrow{\text{Oxid}^n} M^{n+} + ne^- \quad \text{e.g.} \quad Fe \xrightarrow{\text{Oxid}^n} Fe^{2+} + 2e^-$$

$$\frac{1}{2}O_2 + 2e^- \xrightarrow{\text{Red}^n} O^{2-} \qquad \frac{1}{2}O_2 + 2e^- \xrightarrow{\text{Red}^n} O^{2-}$$

$$M^{n+} + O^{2-} \longrightarrow M_2O_n \qquad Fe^{2+} + O^{2-} \longrightarrow FeO$$

The extent of the corrosion, depends upon the type of the oxide film formed by metals. The oxide films formed are classified into three categories.

a) Stable oxide film
   - i) Porous – e.g. Iron Oxide
   - ii) Non-porous – e.g. Oxides of Al, Ni, Cr etc.

b) Unstable oxide film – e.g. Oxides of noble metals

c) Volatile oxide film – e.g. Oxides of molybdenum

Table 2.2.1 : Role of oxide film

Sr. No.	Type of oxide film	Example	Role/ Effect
(a)	Stable oxide film (i) porous oxide film	Iron oxide FeO / Fe_2O_3 / Fe_3O_4.	Being porous film, the corrosion of under lying metal continues. The rate of corrosion slows down.
	(ii) Non-porous	Al_2O_3 Al-oxide	Being non-porous film, the corrosion of underlying metal stops till the film is intact.
(b)	Unstable oxide film	Oxides of noble metals.	Being unstable film, the oxide decomposes and metal surface continues to be exposed. Hence, corrosion of underlying metal continues.
(c)	Volatile oxide film	Oxides of some metals like molybdenum.	Being Volatile oxide, it is lost to environment, leaving fresh metal exposed. Rate of corrosion very high, till entire metal lost.

a) Stable oxide films

Stable oxide films normally get adhered to the underlying metal surface and hence provide a protective layer on surface, thereby reducing rate of further corrosion. But, extent of further corrosion depends upon the type of stable film formed.

(i) Porous oxide layer

If oxide film formed on metal surface is *porous* in nature, the *rate of further corrosion is not reduced* much. This can be understood better by taking example of alkali metals such as Li, Na, K or alkaline earth metals such as Ca, Mg etc. These metals react with oxygen, forming oxide such as Na_2O, K_2O, CaO, MgO, etc. where *volume of oxide formed is less than the volume of reacted metal.* Thus, oxide layer is not able to cover the entire surface of metal block/piece. Hence, in oxide film, *pores are developed.* These *pores give free access* to oxygen, which attacks the underlying pure metal. Thus, *corrosion does not stop* till pure metal is available.

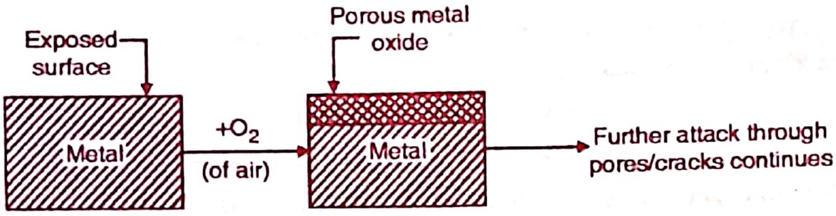


Fig. 2.2.1 : Porous oxide layer

(ii) Non-porous oxide layer

If the oxide film formed is *non-porous in nature*, the *rate of corrosion reduces* considerably and in most of the cases, corrosion of metal stops. The metals like Al, Cr, etc. form their oxides such as Al_2O_3, Cr_2O_3, etc. whose volume is greater than the volume of metals. Hence, the *oxide film formed, covers the underlying metals* completely, *not leaving* any *access for further attack of oxygen*, thereby *stopping further corrosion*. Thus, metals develop a *protective oxide layer* and become *passive* till this layer is uninterrupted.

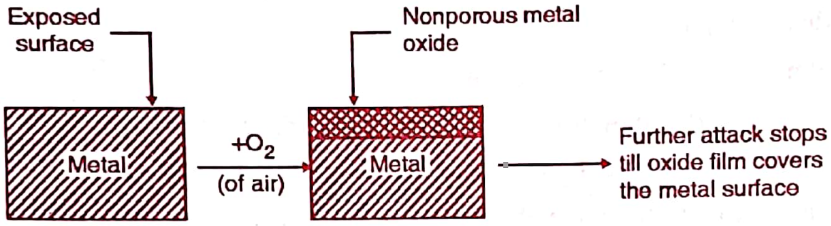

Exposed surface
Nonporous metal oxide
Metal
+O_2
(of air)
Metal
Further attack stops till oxide film covers the metal surface

Fig. 2.2.2 : Non porous oxide layer

b) Unstable oxide films

Unstable oxide films are those which get decomposed on the metal surfaces forming back the metal and oxygen.

Metal + Oxygen → Metal oxide → Metal + Oxygen

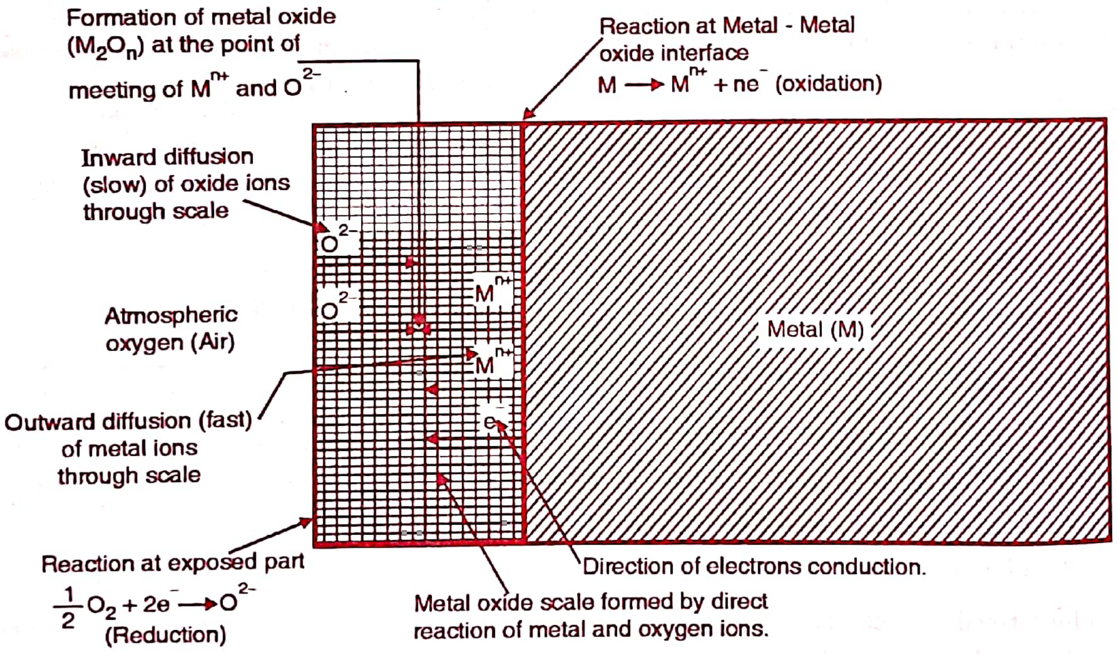

Formation of metal oxide (M_2O_n) at the point of meeting of M^{n+} and O^{2-}
Reaction at Metal - Metal oxide interface
$M \longrightarrow M^{n+} + ne^-$ (oxidation)
Inward diffusion (slow) of oxide ions through scale
O^{2-}
O^{2-}
M^{n+}
M^{n+}
e^-
Atmospheric oxygen (Air)
Metal (M)
Outward diffusion (fast) of metal ions through scale
Reaction at exposed part
$\frac{1}{2}O_2 + 2e^- \longrightarrow O^{2-}$
(Reduction)
Direction of electrons conduction.
Metal oxide scale formed by direct reaction of metal and oxygen ions.

Fig. 2.2.3 : Schematic representation of oxidation mechanism of metals

Example : Oxides of metals like gold, platinum, silver, etc.

Hence, *such metals* forming unstable oxide film *do not get corroded*, but loss of metal continues, slowly.

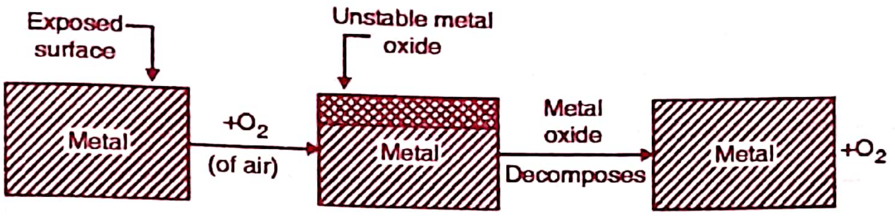


Fig. 2.2.4 : Unstable oxide layer

c) Volatile oxide films

Volatile oxide films are those which get *vaporised* from metal surfaces as soon as they are formed, leaving behind the underlying metal surfaces for further attack of oxygen.

$$\text{Metal} + \text{Oxygen} \rightarrow \text{Metal oxide}$$

For example : *Molybdenum* metal forms its oxide, which is volatile.

Thus, in such cases, *corrosion continues* till the metal is available.

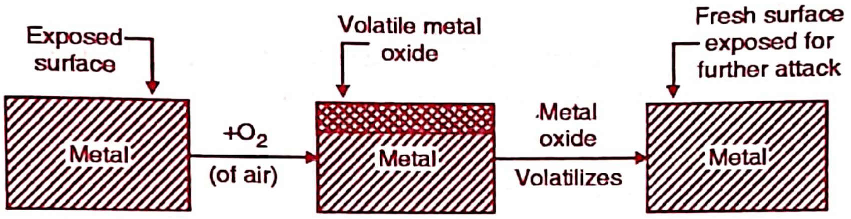


Fig. 2.2.5 : Volatile oxide layer

(ii) Corrosion due to other gases

- Gases such as CO_2, H_2S, SO_2, Cl_2, F_2 etc. react on the metal surface resulting in formation of a film of corresponding compound.
- The extent of corrosion is mainly governed by the chemical affinity of metal and attacking gases. The rate of further corrosion depends upon the volume of the film of corrosion product and the volume of the metal.
- In case of the attack of other gases e.g. Cl_2, the nature of product differs from metal to metal e.g. Cl_2 reacts with *silver* to give highly *protective film* of silver chloride whereas same gas reacts with *tin* to form the corresponding chloride which is *volatile in nature*, as,

  Example : $2\,Ag + Cl_2 \rightarrow 2\,AgCl$ (Protective)

  $Sn + 2\,Cl_2 \rightarrow SnCl_4$ (Volatile)
- Here, the film of *silver chloride* is *protective* (non-porous), hence rate of further corrosion reduces, while that of *stannic chloride is volatile* in nature, hence rate of corrosion is enhanced.
- Thus it is obvious that the corrosion of silver due to the attack of chlorine stops on the surface of metal whereas that of tin continues till the tin metal gets completely vanished.
- Similarly, H_2S attacks the metals like Fe as,

  $$Fe + H_2S_{(aq)} \rightarrow FeS + 2H \text{ (Atomic hydrogen)}$$
- The atomic hydrogen thus formed, penetrates the voids in metal by diffusion, and gets accumulated there, and recombines to form molecular hydrogen,

  $$H + H \rightarrow H_2$$
- As the concentration of molecular hydrogen in voids increases, it causes blisters and fissures in the metal. Thus, strength and ductility of metals reduces considerably. This is known as *hydrogen embrittlement.*
- At high temperature, molecular hydrogen decomposes thermally forming atomic hydrogen, which is highly active and hence reacts with other element present in metal.

- **Example :** Carbon present in steel is available for attack of atomic hydrogen, at high temperature forming methane gas (CH_4). This type of attack is nothing but *intergranular corrosion.* This *causes reduction in strength of metal / alloy, and metal becomes brittle.*

2.2.2 Wet or Electrochemical Corrosion

Q. What is electrochemical corrosion ? **May 16, May 18, 5 Marks**

Q. Explain the electrochemical theory of wet corrosion, giving its mechanism. **Dec. 17, 6 Marks**

Basic principle

- An electrochemical reaction is one which results in the transfer of electrons.
- When metal surface is in immediate contact of *aqueous acidic/alkaline/ neutral/electrolytic solutions,* the short circuited galvanic cells get set all along the surface of metal. This gives rise to corrosion which proceeds by electrochemical principles. In fact,
- Wet corrosion is more common than dry corrosion.
- The co-ordinating metal(s) behave like *galvanic cells* thereby the *part of metal acting as an anode* is consumed while *the other part* which is *acting as a cathode* remains unchanged.
- **Theory :** This type of corrosion occurs, under following conditions,

  (i) Where a conducting liquid is in contact with metal, or

  (ii) Where two dissimilar metals or alloys are either immersed or dipped partially in a solution.
- These type of conditions are always suitable for formation of *separate anodic and cathodic areas* between which the electric current can flow through the conducting solution.
- *At anode,* the liberation of electrons takes place, i.e. *oxidation reaction.* Consequently at anode, *the destruction of metal occurs,* either by dissolving it as metal ions or by converting it into a compound such as its oxide.
- *At cathode,* the absorption of electrons takes place, i.e. *reduction reaction.* These reactions do not affect the part of the metal acting as a cathode, since most of the metals cannot be further reduced.

  Thus, corrosion occurs always at anode.

  ***Reactions :** At anode*

$$\underset{\text{(Metal)}}{M} \longrightarrow \underset{\text{(Metal ion)}}{M^{n+}} + \underset{\text{(Electrons)}}{ne^-}$$

Formation of metal ions (M^{n+}) at anode causes dissolution of metal and free electrons are liberated. These free electrons are consumed in cathodic reactions with either.

(a) Evolution of H_2 gas. Or,

(b) Formation of a product [oxide of metal] due to absorption of O_2 gas.

depending upon the nature of the corrosive environment.

2.2.3 Mechanism of Electrochemical Corrosion/ Wet Corrosion

Q. With the help of a diagram and electrode reactions, explain mechanism of electrochemical corrosion of iron by hydrogen evolution, in acidic medium. **Dec. 15, 5 Marks**

Q. Explain with the help of diagram wet corrosion in neutral medium. **May 17, 6 Marks**

Q. Explain the mechanism of wet corrosion with respect to neutral and alkaline media. **May 19, 6 Marks**

a) Evolution of Hydrogen type

- Corrosion, by this mechanism occurs usually if environment, surrounding to the metal is acidic.
- **Example :** Pipe lines made from iron metal get corroded if industrial waste material, or solutions of non-oxidising acids, is transported through them.

  The following reaction occurs

$$\text{Anode} \xrightarrow[\text{flow}]{\text{Electrons}} \text{cathode}$$

$$Fe \rightarrow Fe^{+2} + 2e^- \longrightarrow 2H^+ + 2e^- \rightarrow H_2$$

Acidic environment

Bulk of the metal

- From above reactions, we can say that the *flow of electrons takes place from the anode to the cathode.* These electrons are gained by cathodic reaction, and at cathode H^+ ions are eliminated as H_2 gas. The overall mechanism can be represented as

$$Fe + 2H^+ \rightarrow Fe^{2+} + H_2$$

- Thus displacement of H_2 ions from acidic solution by metal ions takes place.

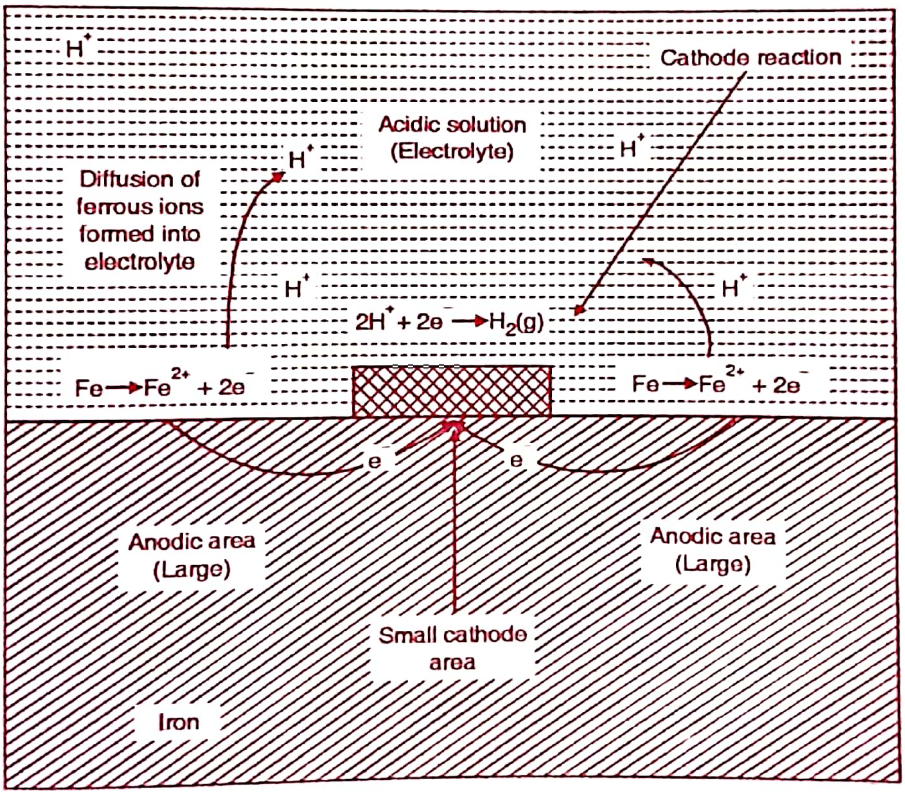


Fig. 2.2.6 : Schematic representation of Mechanism of wet corrosion by hydrogen evolution

- Thus, all metals have tendency to get dissolved in the acidic solution with simultaneous evolution of H_2 gas.

b) Absorption of oxygen type

- **Rusting of iron** in neutral aqueous solution of electrolytes in the presence of atmospheric oxygen is the most common example of this type of corrosion (mechanism).
- Thus, iron metal in such cases is always with a coat of thin film of iron oxide (Fe_2O_3). Since, the film is porous in nature, the surface of iron exposed to atmosphere acts as an anode while rest of surface acts as a cathode.

Anodic reaction

$$Fe \rightarrow Fe^{2+} + 2e^- \text{ (Oxidation)}$$

Thus, at anode iron dissolves as ferrous ions with liberation of electrons.

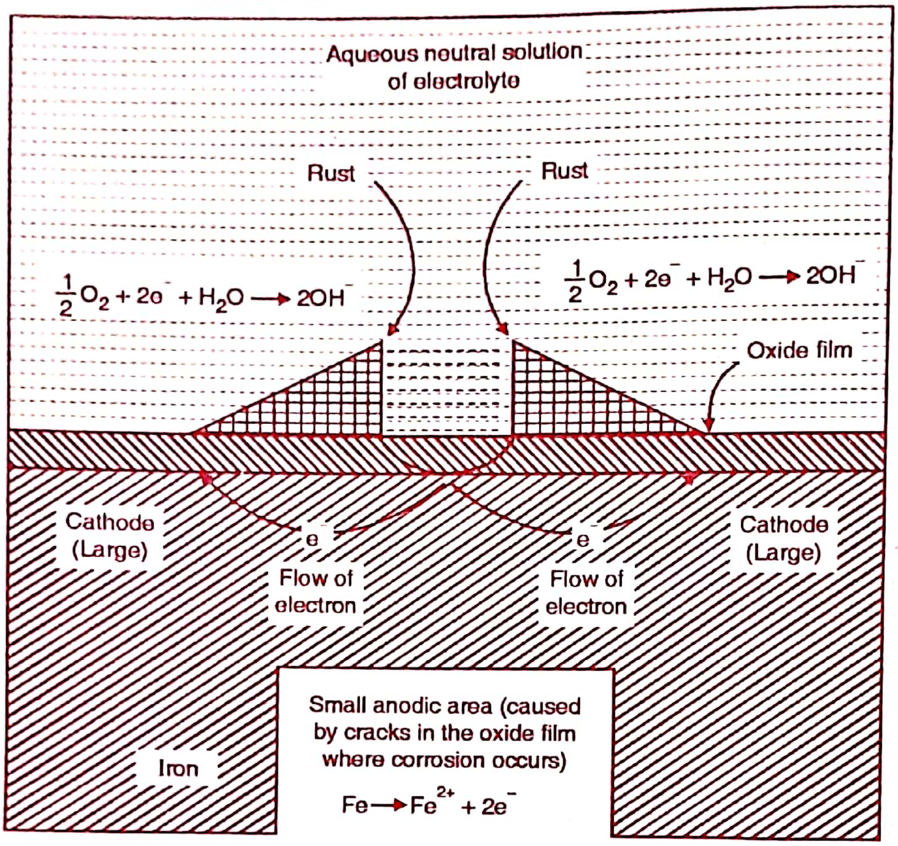

Aqueous neutral solution of electrolyte
Rust
Rust
$\frac{1}{2}O_2 + 2e^- + H_2O \rightarrow 2OH^-$
$\frac{1}{2}O_2 + 2e^- + H_2O \rightarrow 2OH^-$
Oxide film
Cathode (Large)
Cathode (Large)
e
e
Flow of electron
Flow of electron
Small anodic area (caused by cracks in the oxide film where corrosion occurs)
$Fe \rightarrow Fe^{2+} + 2e^-$
Iron

Fig. 2.2.7 : Schematic representation of Mechanism of wet corrosion by oxygen absorption

Cathodic reaction

- The liberated electrons flow through iron metal from anode to the cathode, where electrons are intercepted by the dissolved oxygen as

$$\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^- \text{ (Reduction)}$$

- The Fe^{+2} ions and OH^- ions diffuse and when they meet, $Fe(OH)_2$ is precipitated, as

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 \downarrow$$

Effect of O_2 supply on corrosion product :

- If enough supply of O_2 is available, then $Fe(OH)_2$ readily get oxidized to $Fe(OH)_3$ as

$$4Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4Fe(OH)_3 \downarrow \text{ (yellow Rust)}$$

- This substance is commonly known as *yellow rust* and it actually corresponds to

$$Fe_2O_3H_2O \text{ or } FeO(OH) \text{ and not } Fe(OH)_3$$

- If the supply of oxygen is limited, the product formed may be Ferroso-ferric hydroxide.
- If oxygen supply is increased, cathodic reaction is influenced forming more number of OH^- ions, and subsequently anodic reaction is also influenced, eliminating more number of electrons, thereby increasing the rate of corrosion.

2.2.4 Comparison between Dry and Wet Corrosion

Sr. No.	Dry corrosion	Wet corrosion
1.	It mainly occurs by direct contact of atmospheric gases.	It occurs when metal surface is in immediate contact with aqueous solutions.
2.	The gases are O_2, CO_2, SO_2, H_2S, hydrogen etc.	The aqueous solutions are acids/ alkalis / neutral / electrolytic.
3.	There is no formation of galvanic cells.	Galvanic cells are formed all along the surface of metal being in contact with aqueous solution.
4.	Nature of corrosion product is governed by characteristics of metal.	Nature of corrosion product depends upon medium either with O_2 dissolved or H^+ ions being present.
5.	Mechanism is not explained with electrochemical principles.	Mechanism is explained with electrochemical principle.
6.	Rate of corrosion is governed by nature of corrosion product	Rate of corrosion is governed by cathodic product.
7.	Mechanism	Mechanism
	$\text{Metal} \xrightarrow{\text{oxid}^n} M^{n+} + ne^-$ e.g. $Fe \longrightarrow Fe^2 + 2e^-$ $\frac{1}{2}O_2 + 2e^- \xrightarrow{\text{Red}^n} O^{2-}$ $M^{n+} + O^{2-} \longrightarrow M_2O_n$ $Fe^{2+} + O^{2-} \longrightarrow FeO\downarrow$	At anode $\text{Metal} \xrightarrow{\text{oxid}^n} M^{n+} + ne^-$ e.g. $Fe \longrightarrow Fe^{2+} + 2e^-$ At cathode, $\frac{1}{2}O_2 + H_2O + 2e^- \xrightarrow{\text{Red}^n} 2\,OH^-$ $Fe^2 + 2\,OH^- \longrightarrow Fe\,(OH)_2\downarrow$

2.3 Types of (Examples) of Electrochemical Corrosion

2.3.1 Galvanic Corrosion

Q. Explain Galvanic corrosion with the help of a suitable example and diagram. **Dec. 15, Dec. 18, 4 Marks**

- The *name* of this type of corrosion is *indicative* that there must be formation of a *galvanic cell* on metal surface causing corrosion. Such cells get set up all along the surface of metal when it faces the electrolytic environment and two dissimilar metals in contact.
- For example, in ships floating on the sea water, the portion of it in contact with marine water gets corroded, if there is a difference in the materials used in assembling the ship.
- If metal iron or brass alloy is used together to join various parts, due to difference in potential, a galvanic cell gets set, leading to corrosion.
- In such cases all along the surface of metal small galvanic cells are set up, where *area of high potential acts as an anode and the one with lower potential acts as a cathode.* The portion of metal acting as anode, deteriorates and at cathode the cathodic product gets evolved/deposited, depending upon the environment, and mechanism of the corrosion, i.e. by absorption of oxygen or evolution of hydrogen, as the case may be.

- The case where the former type of mechanism takes place is seen in *electrolytic/alkaline environment* while the latter type is seen in *acidic* environment. The rate of corrosion is obviously very high in latter type. In former one, for iron metal generally three types of iron oxides are formed in succession with the increasing valency of iron. For example : FeO, Fe_2O_3 and Fe_3O_4.
- In such type of environment, on metal surface small anodic and cathodic areas are formed. Here, cathodic area is slightly larger and hence rate of corrosion is comparatively higher. The mechanism of corrosion in slightly alkaline medium, proceeds as, At anode $M \rightarrow M^{2+} + 2e^-$

$$\text{At cathode} \quad \frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^-$$

$$M^{2+} + 2OH^- \rightarrow M(OH)_2 \downarrow$$

- If the metals are surrounded by *aqueous alkaline/acidic/neutral solution*, the mechanism of cathodic reaction proceeds to form OH^- ions, and subsequently $Fe(OH)_2$ or $Fe(OH)_3$.
- If the metal is exposed to acidic medium the mechanism at cathode proceeds to form H_2 gas, while anodic reactions remain the same.
- To avoid the formation of galvanic cells,
  a) The metals should be pure.
  b) The materials used to assemble the different parts should be of same potentials.
  c) Moisture and other electrolytic/aqueous medium, if present, other corrosion controlling methods may be used.

2.3.2 Concentration Cell (Differential Aeration) Corrosion

Q. Write a note on differential aeration corrosion. **May 15, 5 Marks**

- This type of corrosion is due to the *electrochemical attack* on the metal surface, which is exposed to an electrolyte *of varying concentrations* or *of varying aeration*. The variation is caused due to local difference in metal ion concentration caused by,
  (i) Local difference in temperature
  (ii) Inadequate agitation
  (iii) Slow diffusion of metal ions, produced by oxidation at anode.
- It is the most common type of corrosion, and it occurs when one part of the metal is exposed to a different air concentration from the other part. *This causes a difference in potential between differently aerated areas.* It has been found that *poor oxygenated parts are anodic and rest are cathodic.* Consequently, differential aeration of metal causes a flow of current, called *differential current.*
- Example : Metal (Iron) tank/drum storing water or a strip of zinc metal partially dipped in dilute solution of salt; like NaCl and if solution is not agitated properly then the parts of the strip above and closely adjacent to the water line are more strongly aerated; because they have more supply of oxygen while remaining parts of the same strip which are immersed to greater depth have less supply of oxygen and these are poorly aerated and show lower oxygen concentration or lesser access of oxygen, and thus they become anodic. Thus, difference of potential is created which causes a flow of current between the two differently aerated areas of the same metal. Zinc will dissolve at anodic areas as,

$$Zn \rightarrow Zn^{2+} + 2e^- \text{ (Oxidation)}$$

O_2 will take up electrons at the cathodic areas to form OH^- ions.

$$\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^- \text{ (Reduction)}$$

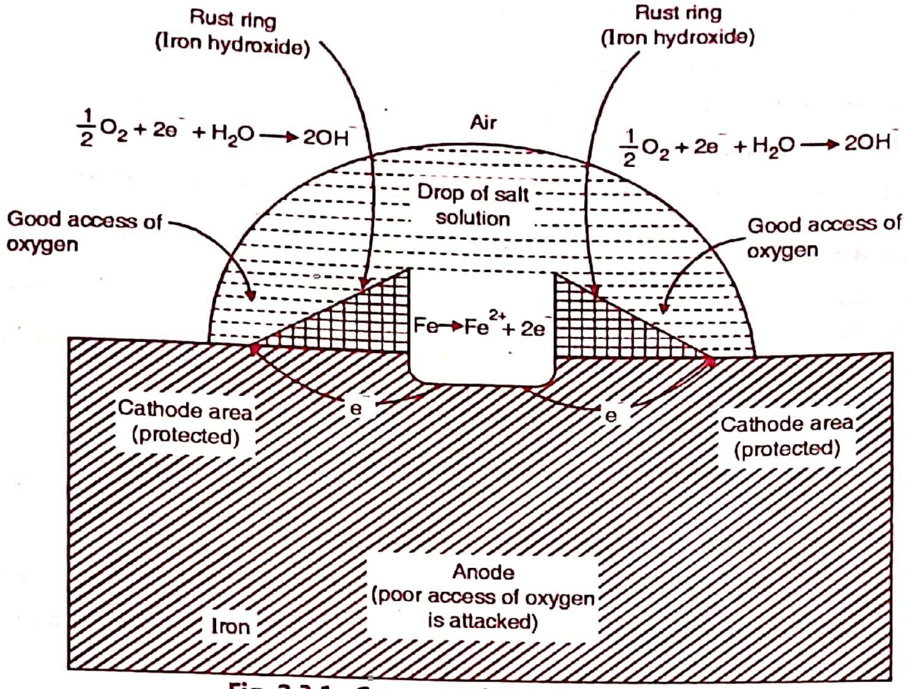


Fig. 2.3.1 : Concentration cell corrosion

2.3.3 Pitting Corrosion

- When metal surface coats / protective film on a metal breaks down, pin holes / pits / cavities are formed.
- Around such pits, small anodic and large cathodic areas are formed. Due to this corrosion is accelerated in localized area, known as "pitting corrosion".
- Such pits are formed due to,
  (a) Local strain, due to alternating or non-uniform stresses, on metal.
  (b) Improper finish - surface roughness.
  (c) Scratches due to friction or sliding under heavy load.
  (d) Severe action of some chemicals or solutions.
- When such metal encounters appropriate environment, corrosion current arises. Fig. 2.3.2 represents schematically, pitting corrosion due to differential aeration, around the area of "pit" on metal surface.
- The small part under drop of water / impurity acts as an "anode" and surrounding large area acts as "cathode". This type of corrosion proceeds continuously with increasing rate [After formation of "pit"].

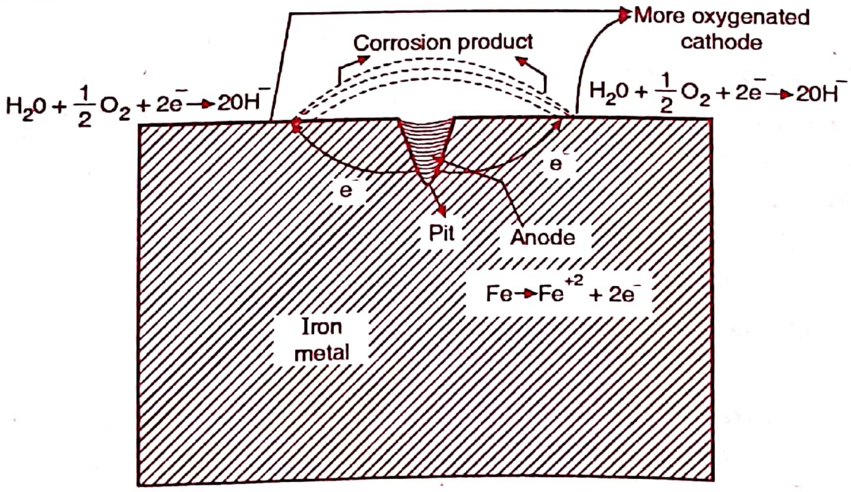

More oxygenated cathode
Corrosion product
$H_2O + \frac{1}{2}O_2 + 2e^- \rightarrow 2OH^-$
$H_2O + \frac{1}{2}O_2 + 2e^- \rightarrow 2OH^-$
e
e
Pit
Anode
$Fe \rightarrow Fe^{+2} + 2e^-$
Iron metal

Fig. 2.3.2 : Pitting corrosion on Iron surface

- Pitting corrosion can be controlled/minimized by,
  (1) By finishing metal surfaces properly.
  (2) By maintaining metal coating intact.
  (3) By using lubricants to control friction.
  (4) By avoiding unwanted contact with corroding solutions / dust / dirt / impurities.

2.3.4 Intergranular Corrosion

Q. Explain intergranular corrosion with a suitable diagram and example. **May 16. 4 Marks**

- This type of corrosion occurs along grain boundaries under following conditions
  (i) the material, highly sensitive to corrosive attack and
  (ii) corrosive liquid possesses *a selective character of attacking only at the grain boundaries*, but leaving the grain centres (interiors) untouched or only slightly attacked.
- This type of corrosion is due to the fact that the grain boundaries contain material, which shows electrode potential more anodic than that of the grain centre in the particular corroding medium. This may be due to precipitation of certain compounds at the grain boundaries,
- Due to such disproportionated precipitation, a solid solution is aggregated at centre, adjacent to boundary.
- The solid solution thus formed is *anodic* with respect to the grain centres as well as to the precipitated compound. Hence it gets attacked preferentially in the corrosive environment (see Fig. 2.3.3).

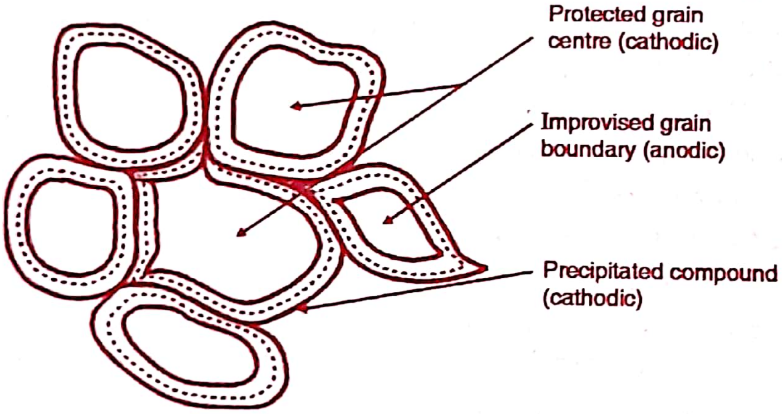

Protected grain centre (cathodic)
Improvised grain boundary (anodic)
Precipitated compound (cathodic)

Fig. 2.3.3 : General intergranular attack

- This type of corrosion is, generally, observed in alloys. For example : during the welding of stainless steel (an alloy of Fe, C and Cr), chromium carbide is precipitated at the grain boundaries.
- Hence chromium composition adjacent to grain boundaries is increased and is more anodic with respect to the solid solution within the grain (which is richer in chromium) and it is also anodic to the particles of the chromium carbide so-precipitated.
- Intergranular corrosion is observed to occur near the grain boundaries and occurs on microscopic scale, without any apparent external signs of any intensive attack.
- On account of this, sudden failure of material occurs (without any pre-warning), due to loss of cohesion between grains.
- The remedy is *proper heat-treatment*, followed by rapid quenching to avoid the heterogeneous precipitation that, usually, occurs due to slow-cooling (annealing).

2.3.5 Stress Corrosion

Q. Define Stress corrosion with an example. **Dec. 18, 2 Marks**

- It is similar to intergranular corrosion.
- Stress corrosion (or stress cracking) "is the combined effect of static tensile stresses and the corrosive environment on a metal."
- It is characterized by a highly localized attack which occurs even when overall corrosion is negligible.
- For stress corrosion to occur the essential conditions are : (i) presence of tensile stress, and (ii) a specific corrosive environment.
- The specific substances act as the corrosive agents and are selective for particular material in particular environment,
- For example (a) caustic alkalis and strong nitrate solution for mild steel; (b) traces of ammonia for brass; (c) acid chloride solution for stainless steel.

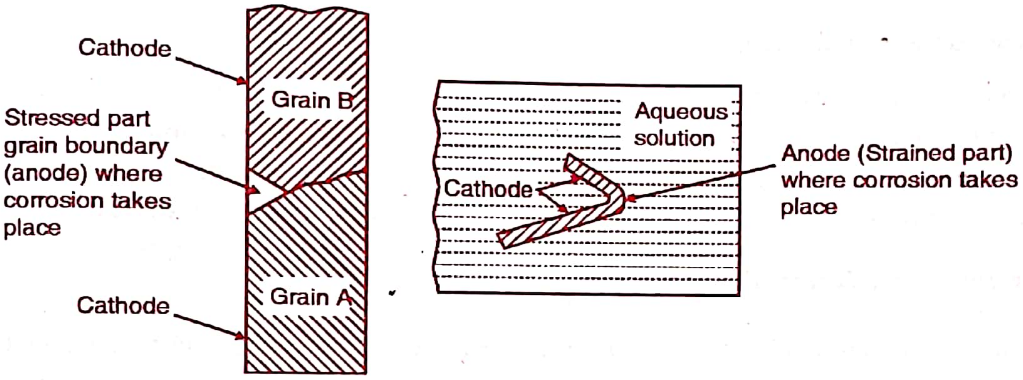

Cathode
Grain B
Stressed part grain boundary (anode) where corrosion takes place
Grain A
Cathode
Aqueous solution
Cathode
Anode (Strained part) where corrosion takes place

Fig. 2.3.4 : Stress corrosion

- This type of corrosion is seen in fabricated articles of certain alloys (like high-zinc brasses and nickel brasses) due to the presence of stresses caused by heavy working like rolling, drawing or insufficient annealing.
- The pure metals are relatively immune to stress corrosion.
- Stress corrosion involves in a localized electrochemical corrosion, forming anodic areas with respect to the more cathodic areas at the metal surface.
- Presence of stress produces strains, which result in localized zones of higher electrode potential.
- These chemically-active sites are attacked, even by a mild corrosive environment.
- This results in the formation of a crack, which grows and propagates in a plant.
- The attack of corrosion continues till failure of structure occurs.
- Some typical examples of stress corrosion are given below :

  1) **Seasonal cracking** is a term applied to stress corrosion of copper alloys, mainly brasses. Pure copper is immune to stress corrosion, but presence of small amounts of alloying element (like P, As, Sb, Zn, Al, Si) result in marked sensitivity. For examples, alpha brass (which when highly stressed) undergo intergranular cracking in an atmosphere, containing traces of ammonia or amines.
  2) **Caustic embrittlement :** Caustic embrittlement is another example in this type of corrosion. Boiler-water, usually, contains a certain proportion of *sodium carbonate*, added for water hardening purposes. In *high-pressure boilers, this breaks up to give sodium hydroxide and carbon dioxide.*

$$Na_2CO_3 + H_2O \longrightarrow 2\ NaOH + CO_2 \uparrow$$

- NaOH makes boiler-water *alkaline*. This very dilute alkaline boiler-water (in boiler) flows through the minute hair-cracks and crevices (by capillary action).

- The water evaporates and the caustic soda concentration builds up in the crevices.
- This concentrated alkali reacts with iron to form sodium ferroate (hypoferrite) which gets deposited in crevices, cracks. Hence, the metal is stressed.
- The sodium ferroate (Na_2FeO_2) then decomposes, according to either of the following reactions :

$$3Na_2FeO_2 + 4H_2O \longrightarrow 6\ NaOH + Fe_3O_4 + H_2$$

$$6Na_2FeO_2 + 6H_2O + O_2 \longrightarrow 12\ NaOH + 2\ Fe_2O_4$$

- Sodium hydroxide is regenerated and magnetite (Fe_3O_4) is precipitated, thereby enhancing further dissolution of iron.
- *Caustic embrittlement* can be explained by considering the following electrochemical cell :

$$^{+}\text{Iron} \mid \text{Concentrated NaOH} \mid \text{Dilute NaOH} \mid \text{Iron}^{-}$$

- The iron surrounded by the dilute NaOH (main body) is the *cathodic side*; while the iron in contact with more concentrated caustic soda (e.g., crevices, hair-cracks, rivets) is the *anodic portion*, undergoing corrosion and is thus dissolved.

Prevention of caustic embrittlement

- It can be prevented by "Internal conditioning".
- The best is addition of sodium sulphate to the boiler-water. Another is to use tannin or lignin as additive to the boiler-water. Both these methods prevent caustic cracking by blocking up the hair-cracks and crevices with inocuous harmless substances, thereby preventing the sodium hydroxide from infiltrating.

2.3.6 Polarization of Electrodes

- The driving force of an electrochemical corrosion process is the potential difference between the anode and the cathode.
- The corrosion rate is controlled by the current flowing in the circuit.
- The addition of certain inorganic or organic substances (called inhibitors) to the corroding environment reduces the extent of corrosion.
- These inhibitors cause certain irreversible changes around the electrodes.
- Such changes tend to oppose the direction of the corrosion current flow.
- This phenomenon is called polarization of electrodes which alters makes the cathode to be less cathodic (or more anodic) and that of the anode to be less anodic (or more cathodic).
- As a result of this, the potential difference and current between the anodic and cathodic areas decreases, thereby the corrosion rate also decreases.
- Polarization at the electrodes is due to : (i) concentration changes in the electrode region, (ii) overvoltage or (iii) presence of surface films on the electrodes.
- Generally, the concentration of corrosive electrolyte species gets accumulated at the anode and depleted at the cathode. This in turn creates a concentration difference between the bulk of the corrosive electrolyte and the electrode surface.
- Now for corrosion reaction to progress, the electrolyte species must be supplied around the electrode depleted with respect to electrolyte species or removed around the electrode concentrated with respect to electrolyte continuously.
- Both these processes (of supplying or removing electrolyte species) occur by diffusion.
- The diffusion becomes sluggish in (i) stagnant situations, (ii) low concentration of the electrolyte species and (iii) low temperature.

- Such delayed diffusion has a tendency to *polarize electrodes*, thereby decreasing *corrosion current* and *corrosion rate.*
- As the corrosion reaction progresses, the potential difference between the anodic and cathodic areas alters and ultimately as steady state, called *corrosion potential* (E_{corr}) is reached, when the sum of the rates of all anodic (oxidation) reactions become equal to the sum of the rates of all cathodic (reduction) reactions.
- The corresponding values of current at this potential, is called corrosion current (I_{corr}), whose value depends on :

(i) The current densities at the anode and cathode,

(ii) Potential difference between the anode and the cathode,

(iii) Relative areas of the anode and cathode,

(iv) Polarization characteristics of anode as well as cathode and temperature.

Thus, I_{corr} = Anodic current density (I_a) − Cathodic current density(I_c)

(v) If the cathode area is larger than the anode area, then,

$$I_a > I_c$$

$\therefore$ I_{corr} is positive

$\therefore$ Material undergoes corrosion at higher rate.

(vi) The *greater* the extent of polarization of either anode or cathode or both, the *smaller* is the corrosion current and hence, *lower* is the corrosion rate.

(vii) Corrosion rate is lower at *lower* temperature, since the diffusion process is *retarded.*

2.4 Factors Influencing Rate of Corrosion

Q. How the rate of corrosion influenced by following factors.

(i) Overvoltage

(ii) Purity of metal **May 15, Dec. 15, May 16, 2 Marks**

Q. How the rate of corrosion influenced by following factors.

(i) PH of medium.

(ii) Nature of corrosion products. **May 15, Dec. 15, May 17, Dec. 17, Dec. 18, 2 Marks**

Q. Explain the factors affecting the rate of corrosion relative areas of anode and cathode. **May 17, 2 Marks**

Q. Explain the factors affect the rate of corrosion - Position of metal in galvanic series. **Dec. 17, 2 Marks**

1. Nature of Metal

Nature of metal depends upon its position in galvanic series and potential difference.

2. Position of Metal in the Galvanic Series

This is a major factor for corrosion of metals. If two dissimilar metals are in corroding environment, the metal having higher electrode potential and position in the galvanic series undergoes corrosion, i.e. it acts as an anode.

3. Potential Difference

Amongst the two metals in contact, greater the difference in the electrode potential, higher is the rate of corrosion.

4. Overvoltage

When a metal, which occupies a high position in galvanic series (say zinc), is placed in 1N-H_2SO_4, it undergoes corrosion forming a film and evolving hydrogen gas.

The initial rate of reaction is quite slow, because of high overvoltage (= 0.70 V) of zinc metal, which reduces the effective electrode potential to a small value.

If a few drops of copper sulphate ($CuSO_4$) are added, the corrosion rate of zinc is accelerated, because some copper gets deposited on the zinc metal, forming *minute cathodes*, where the hydrogen overvoltage is only 0.33 V. *Thus, reduction in overvoltage of the corroding metal/alloy accelerates the corrosion rate.*

"The difference between the potential of the electrode when the gas evolution was actually observed and the theoretical reversible value of the same solution is called the overvoltage or over potential".

5. Areas Occupied by the Anode and Cathode

If two *dissimilar* metals are in contact, one forming anode while another forming cathode, then the corrosion of the anodic metal (part) is directly proportional to the ratio of the areas occupied by the cathode and anode.

$$\text{Thus, corrosion at anode } \alpha = \frac{\text{Area of cathodic part}}{\text{Area of anodic part}}$$

Hence, if cathode is large and anode is small, then corrosion at anode is higher and vice-versa.

6. Purity of the Metal

- If the metals are impure, then the impurities present in them cause heterogeneity, which *gives rise to small electro-chemical cells* at the sites where metal and impurities are exposed, to the corrosive environment and thus, the corrosion starts, which then affects the entire metal.
- **Example :** Zinc metal, if with the impurities of Fe or Pb, undergoes corrosion at the sites where the impurities are exposed because of the formation of local small electrochemical cell. *Thus more the percentage of impurity, higher is the corrosion of zinc metal.*

7. Nature of Corrosion Product

Note : All students to, Entire description under chemical corrosion should be referred and included for this point (Refer to Sec. 2.2.1.).

8. Temperature

The rate of corrosion is greater at higher temperature, because diffusion of gases increases with the rise in temperature. Another example of increase of corrosion with rising temperature is *caustic embrittlement* as observed in boiler.

9. Moisture

The corrosion also is found to enhance in humid air as compared to in dry air. This is because, humid air/moist air has tendency to dissolve gases such as O_2, CO_2 etc. and also the acidic vapours from industries. Due to this, it becomes easy to set up an electrochemical cell on the surface of metal. Some metals like Mn, Cr, Fe, Mg etc. get corroded in moist air, even in the absence of oxygen, forming few other compounds.

10. Influence of pH

In acidic, pH, the rate of corrosion is higher, because the mechanism of electrochemical corrosion proceeds by evolution of hydrogen gas at cathode. On the contrary, in alkaline or neutral electrolytic medium the electrochemical corrosion occurs by following the mechanism of absorption of oxygen; thereby forming an oxide film as a cathodic product. Such a film gets adhered to the surface of the metal and further rate of corrosion is governed by *nature of the corrosion product* which is discussed earlier.

11. Concentration of Electrolyte

- *Presence of other ions* also influences the rate of corrosion. For example : if in vicinity of metal, Cl^- ions are present, the effect is so severe that even a passive surface film of metal gets destroyed by Cl^- and corrosion starts, on the exposed metal surface.

- *Another example is of metal copper present in mine water.* When such mine water is transported in iron pipes, presence of copper which is less electropositive than iron, influences the formation of galvanic cell and thereby the iron pipes get corroded at a very high rate.
- In fact each and every metal shows its own characteristic behaviour. The amazing behaviour of magnesium metal is worth noting. The presence of N/10 NaCl makes magnesium to corrode while strong KOH solution does not affect the metal.

12. Concentration of Medium

- When the metal is in vicinity of acidic medium, the rate of corrosion increases. This is due to H⊕ ions are increased. The rate of corrosion decreases with rise in pH. If H+ ions increase, pH falls, corrosion increases.
- When metal is having medium with high concentration of oxygen, corrosion rate increases.
- When metal is facing higher temperature of medium, corrosion rate increases.
- When metal is surrounded by difference in concentration of medium rate is influenced. E.g. waterline corrosion.
- When chloride ions are in vicinity of metal, the rate of corrosion rises.
- When metal is in vicinity of saline water, rate of corrosion is higher.

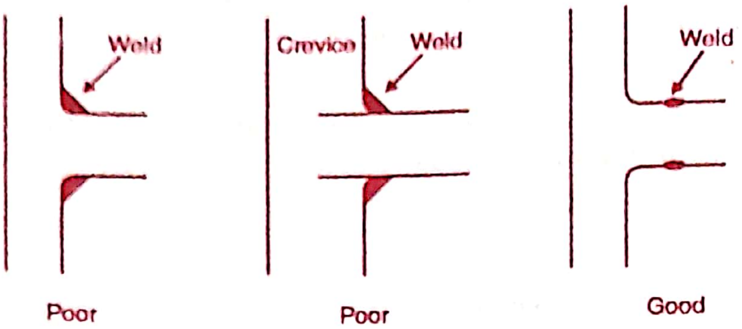
2.5 Methods to Decrease Rate of Corrosion

- '*Corrosion*' is one of the major causes of increasing maintenance cost in all the industries, therefore either prevention or subsequent control of corrosion becomes all the more important.
- The methods for corrosion control vary from condition to condition, because as we have discussed, the types of corrosion are many and conditions under which corrosion occurs also differ to wider extent. *This makes it difficult to apply any single method to solve the problem.*
- The methods to prevent the corrosion are as follows :

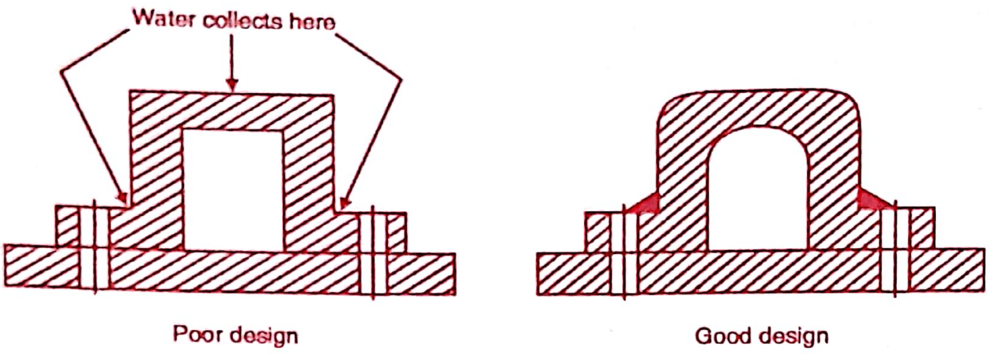
1) Proper designing.
2) Using Pure metal.
3) Using metal alloys.
4) Cathodic protection.
   i) Sacrificial anodic protection.
   ii) Impressed current method.
5) Anodic protection method.
6) Application of protective coatings.
   a) Metallic coating.
   b) Nonmetallic coating.

2.5.1 Proper Designing

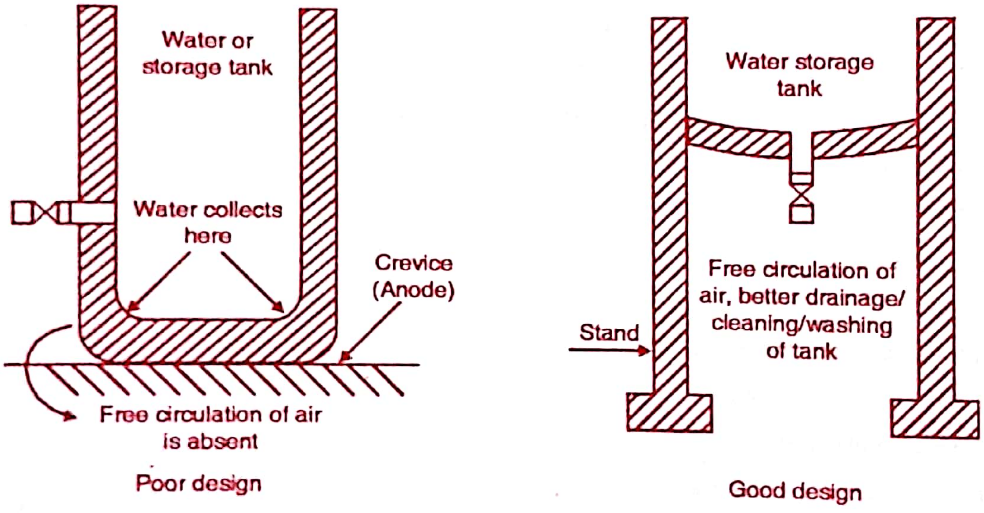
- Designing of the parts should be such that it avoids sharp bends, stresses, etc. or as far as possible the use of screws, nuts, bolts should be avoided, rather welding should be preferred; or the material selections should be in such a way that potential difference does not exist to greater extent.
- The surfaces of two joining parts should be as smooth as possible, so that crevices are as thin as possible, which avoids accumulation of the corrosive liquids, suspended particles, dust dirt, grit stagnation of water, free circulation of air, etc.



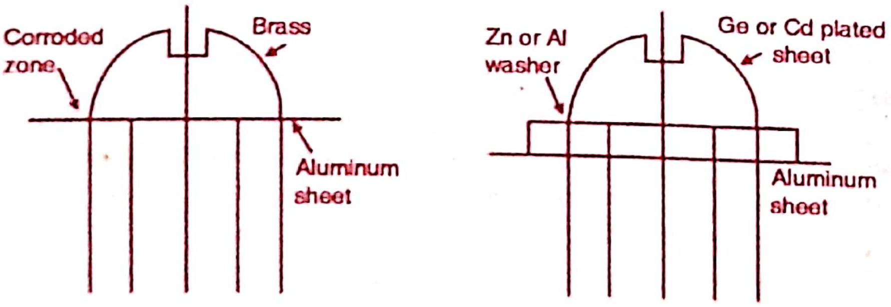
(a) Sharp corners and recesses to be avoided



(b) Avoidance of water stagnation and crevice corrosion

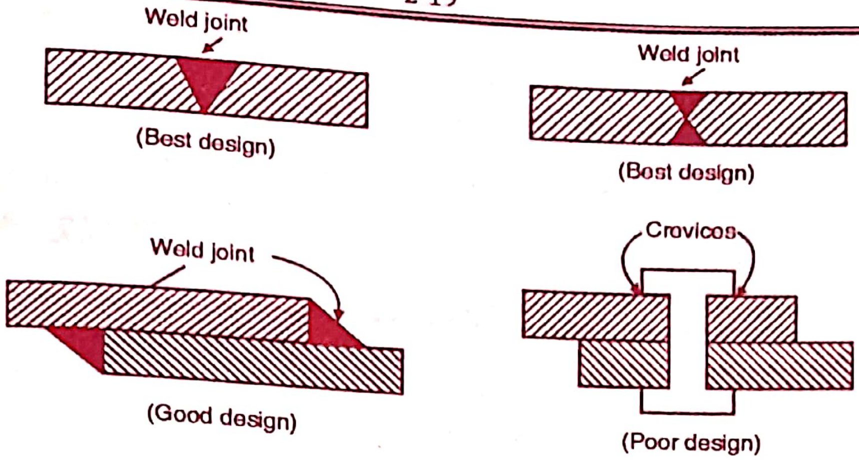


(c) Storage containers

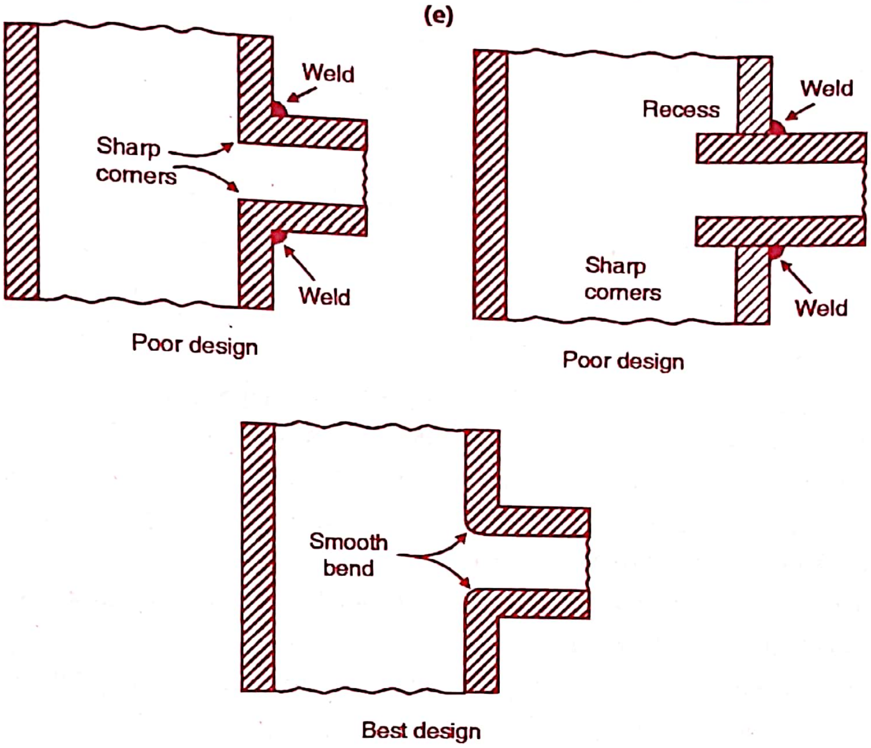


(d) Materials for joining parts

Fig. 2.5.1 : Control of corrosion by proper designing and material selection



(e)



(f)

Fig. 2.5.1 : Control of corrosion by proper designing and material selection

2.5.2 Using Pure Metal

If the metal used to manufacture machine parts is 100% pure, the corrosion resistance is more as compared to the impure metal. This is because, impurities cause heterogeneity. Thus, use of pure metal or purifying the metals prevents corrosion. This method is useful only if corrosion proceeds by electrochemical mechanism.

2.5.3 Using Metal Alloys

- Corrosion resistance of metals can be improved by alloying the metals. Alloying can help to greater extent, if it gives homogeneous product.
- **Example :** Iron can be alloyed with chromium and carbon to give steel, which has better corrosion resistance. Here, chromium metal has a tendency to form an oxide which gets adhered to the surface. Also, this oxide film, if broken gets healed immediately. Thus, steels containing 13% chromium are normally used to make cutlery, surgical instruments, springs, etc. while higher percentage of chromium such as upto 25% are used to prepare turbine brackets, heat resisting parts etc.

- Brass is another example. Individually, copper or zinc are less resistant to corrosion, but alloy of these two metals possesses better resistance to the corrosion.

2.5.4 Cathodic Protection Method

Q. What is cathodic protection ? **May 15, May 18, 6 Marks**

Q. Explain the method of impressed current cathodic protection. **May 15, May 17, Dec. 17, 3 Marks**

Q. Discuss in brief sacrificial anode method of corrosion protection. **Dec. 17, 3 Marks**

- Cathodic protection is nothing but a method used to reverse the flow of current between the two dissimilar metals, under corroding environment thereby reversing the action of the metals in contact. This is achieved by applying the external circuit and forcing the anodic metal to behave as a cathode.
- Anodic protection involves suppression of anodic reaction by adjusting the potential of the more reactive metal, i.e. making metal passive in the working environment.

Methods of cathodic protections

- Cathodic protection can be achieved by two different method as :
  i) By using sacrificial anode method/Auxiliary anode method
  ii) By using impressed current method.
- Both the methods are discussed here in detail.

(i) Use of sacrificial anode

- To achieve protection by *sacrificial anode* method, the metal to be protected from corrosion is *connected by a wire* to another piece of metal which is *more reactive* than the *base metal* itself.
- This results in the corrosion of the piece of metal connected, thereby saving base metal.
- Since the more active metal sacrifices itself, by undergoing corrosion and saving the base metal, *the method is named as sacrificial anode or auxiliary anode method.*
- When the piece of more active metal gets corroded completely, it is simply replaced by new piece.
- The metals normally used are Mg, Zn or Al.
- This method is used normally to protect pipelines carrying water or industrial wastes, and which are normally embedded under the soil, thereby facing the conditions of soil corrosion as well as microbiological corrosion.
- Applications of this method are seen to protect *cables or iron pipelines*, by connecting them to *Mg-blocks*; and in case of *marine structures, ships are protected by using Zn-plates* as sacrificial anode. Even *water tanks, boilers* are protected by using *Zn metal.*

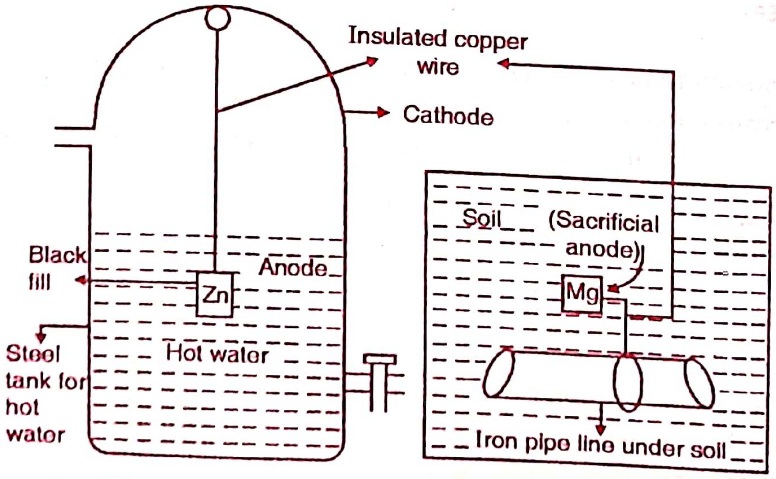


Fig. 2.5.2 : Corrosion control by sacrificial anode method

(ii) Use of impressed current

- In impressed current method, a current is applied in the opposite direction to that of corrosion current, thereby nullifying the effect of the latter one on the base metal, i.e. converting the base metal, to cathode from an anode.
- Such an impressed current can be obtained by using *d.c. source such as battery or dry cell* along with an insoluble anode such as *platinum, stainless-steel, graphite etc.*

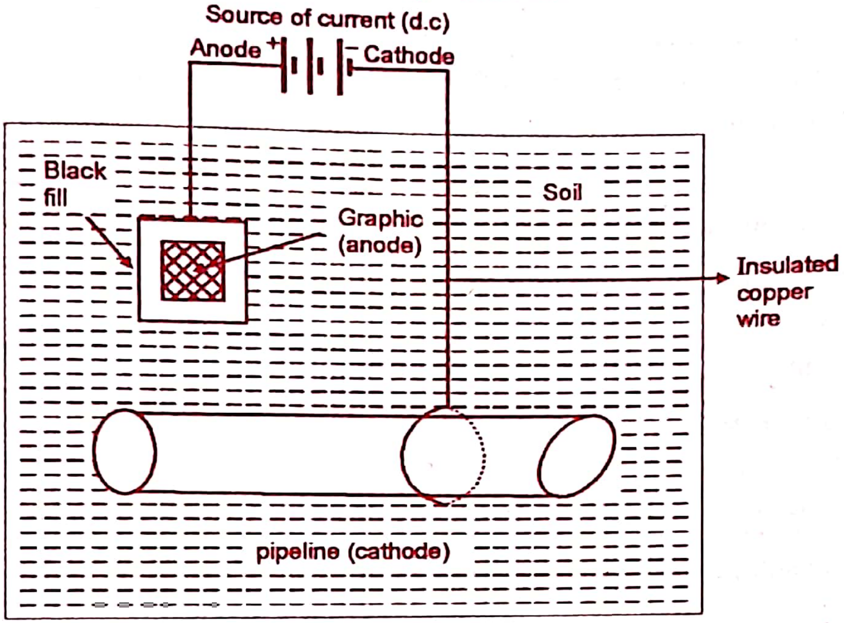


Fig. 2.5.3 : Corrosion control by impressed current method

- In this method, as shown in Fig. 2.5.3, the insoluble anodic metal used (i.e. platinum, steel, scrap iron etc.) is normally *embedded underground*. To this, with the help of d.c. current source, the impressed current is applied, and whole of this assembly is connected to the metallic structure to be protected.
- The connections are done by using wires.
- The insoluble anode is kept inside back-fill made up of *gypsum or any such material*, which can help in increasing the electrical contact with the soil.
- Such an anode can be single, if the area of the metallic structure to be protected is small.
- There can be many such anodes, *connected in series* if the area of the metallic structure to be protected is wider, i.e. long pipeline etc.

Advantages

i) This method is highly useful, because it can protect the long length structures for a long term, thereby reducing frequency of monitoring as well as maintenance cost.

ii) These both methods are most widely used, because the protection provided to the base metal is long term and maintenance is easy.

Disadvantage

Due to the application of the impressed current, the anode deteriorates and hence, it has to be replaced from time to time.

Application

This method are seen in the case of water tanks, buried pipe lines carrying water or oil, condensers, transmission line towers, laid-up ships, etc.

2.5.4(A) Comparison between Cathodic and Anodic Protection

Sr. No.	Cathodic protection	Anodic protection
1.	The basic principle "is to force the metal to be protected to behave like a cathode."	The basic principle is, "to increase the passivity of the base metal by applying current in the direction in which the metal would become more anodic."
2.	The cathodic protection involves reverse the flow of current between two dissimilar metals.	The Anodic protection involves suppression of anodic reaction by adjusting the potential of the more reactive metal i.e. making metal passive.
3.	The cathodic protection can be achieved by two different techniques (a) Sacrificial anode (b) Impressed current	There are no different techniques for anodic protection.
4.	In this method, either Mg, Zn or Al is used as sacrificial anode. It can be applied to most of metals to protect form corrosion.	No such sacrificial anode used, but passivity of metal is increased at low current density. It is necessary to have passive base metal.
5.	It can protect long length structures for long term.	It can protect complicated structures over wide range of corroding environment.
6.	It is not very costly.	The initial cost is high, though operating cost is low.
7.	It can provide steady, consistent protection for long term.	It may not provide steady protection; If system goes out of control, the rate of corrosion may increase suddenly.

2.5.5 Anodic Protection Method

Q. Distinguish between anodic protection and cathodic protection. **May 17, 2 Marks**

Q. What is anodic protection method of corrosion control? Explain with the help of a neat diagram. **May 19, 6 Marks**

- This method to protect base metal is used under certain conditions, such as, where metal to be protected possesses active passivity. e.g. stainless steel.
- The principle involved is to increase the passivity of the base metal by applying current in the direction in which the metal would become more anodic.
- The important factors which *influence* this method can be summarized as below :
  - i) The metal to be protected should possess high passivity, over wider range of potential.
  - ii) The passivity should be increased at low current density, thereby reducing the cost.
  - iii) The cathodic metal used should possess adequate resistance to corrosion under working conditions. Generally, platinum clad metals or other corrosion resistant alloys are used.
- By using *anodic protection* technique, the complicated metal structures can be protected, because *the method is highly effective,* if proper selection is done in choosing cathodic metal for a given set of working conditions.

Advantages

i) Operating cost is low.
ii) Wide range of corroding environments can be tackled.
iii) Complicated metallic structures can be protected.
iv) The applicability of method can be checked in laboratory on small scale and use of cathodic metal can be fixed by trial and error techniques, before going on large scale.
v) During operation, from protection current density, rate of corrosion can be known.

Disadvantages

i) Method is useful only for metals showing *passivity.*
ii) Initial cost of installation is high, due to use of high-starting current, reference electrode, auxiliary electrode and a potentiostat.
iii) If system goes out of control, the rate of corrosion increases suddenly.

2.5.6 Selection of Metal

- For selection of right material of construction, the material should be
  a) High mechanical strength
  b) High corrosion resistance
  c) Low cost
- The material is selected by checking
  i) Its availability
  ii) Safety
  iii) Impurities
  iv) Excess temperature, pressure or agitation etc. is checked.
- Other parameters to be considered is
  i) Maintenance cost
  ii) Life of material
  iii) Cost

2.5.7 Use of Corrosion Inhibitors

- These are the substances added in small quantities (e.g. 0.1%) to the corrosive medium. This stops or slows the electrochemical corrosion.
- These corrosion inhibitors follow following mechanism.
- Inhibitor substances get adsorbed on metal surface.
- The form a layer and combine with corrosive film and protect metal surface.
- They form coating on metal surface and protect.

Types of inhibitors :

These are of two types

i) Inorganic
ii) Organic

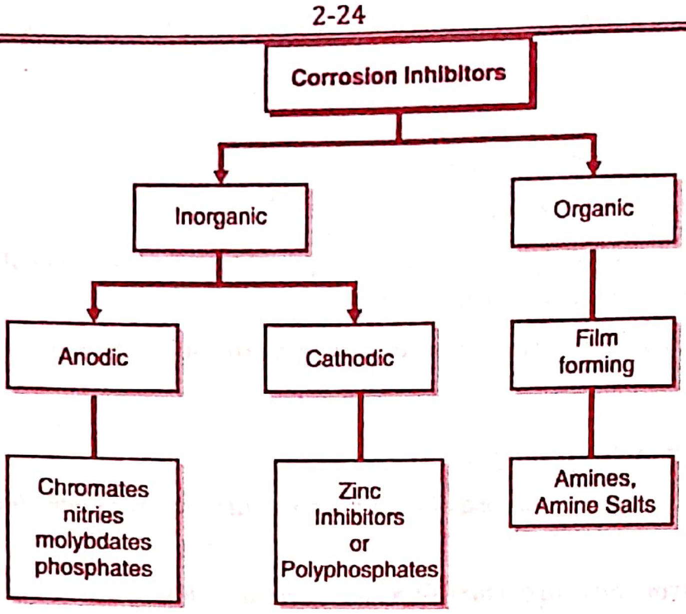


Fig. 2.5.4

i) Inorganic

Used in boilers, cooling towers and fractionating units.

Inorganic inhibitors are further divided into : Anodic and cathodic.

ii) Organic

Used in oil field systems.

2.6 Application of Protective Coatings

This method is most easy and effective of all the methods discussed earlier, for the simple reasons, that it can provide a continuous barrier between the metal surface and the corrosive environment. The problem of localized corrosion starts only when the protective coat gets broken, due to friction or by any other wear and tear of metal surface.

Types of protective coatings :

There are mainly two types of protective coatings.

(a) Metallic coatings

(b) Non-metallic coatings

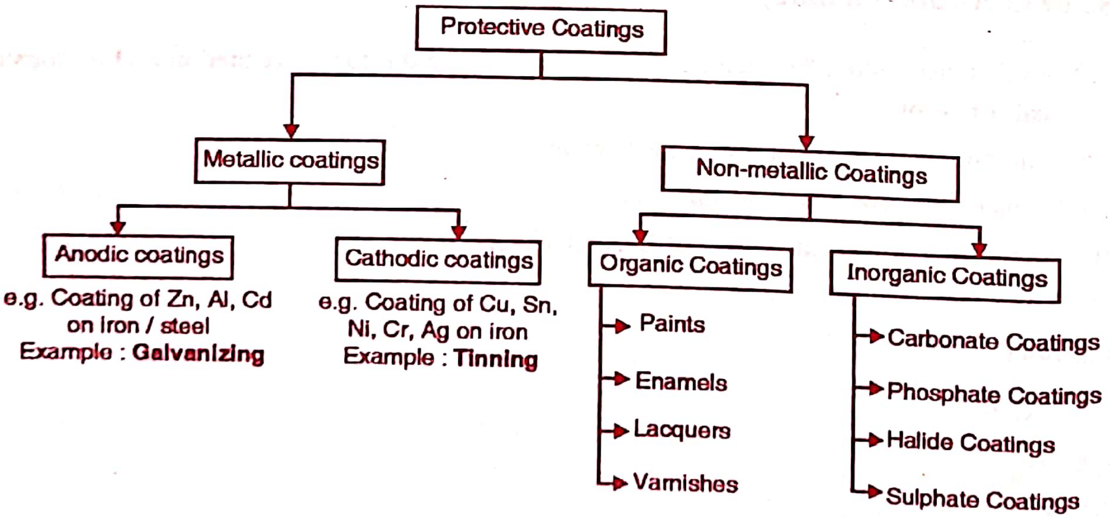


Fig. 2.6.1

2.6.1 Metallic Coatings

Q. What are metallic coatings ? **May 16, 2 Marks**

Q. Name the different methods of applications of metallic coatings. **Dec. 18, 3 Marks**

- Methods of cleaning and preparation of metal surfaces

(1) Solvent cleaning	(2) Acid cleaning
(3) Chemical cleaning	(4) Alkali cleaning
(5) Mechanical cleaning	(6) Flame cleaning
(7) Sand blasting	(8) Acid pickling and etching

- This type of coatings are either anodic or cathodic depending upon the electrode potential of base metal and coating metal.

(1) Anodic coatings

- Metals like *Zn, Al or Cd*, if coated on iron or steel, serve as *anodic coatings*, because their electrode potentials are higher than the base metal.
- Here, as long as coat layer is intact, the corrosion of base metal is totally under control, but in case any *pores, cuts or breaks* occur, there is a formation of galvanic cell, between the coated metal portion and the exposed base metal portion.

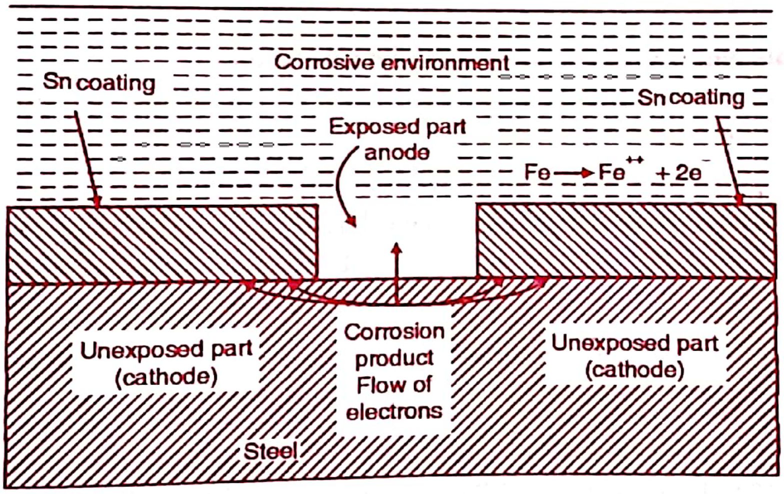


Fig. 2.6.2 : Corrosion of base metal due of broken anodic coatings (Schematic representation)

- In the case of galvanized steel, where Zn is coated on iron (steel), if coating of zinc is broken due to stress or friction, galvanic cell originates. As Zn is anodic to iron, it dissolves and hence iron is protected even though cell is set up and *iron remains protected* till entire amount of zinc gets dissolved.

(2) Cathodic coatings

- In case of *cathodic coatings*, a coat of more noble metal is applied on the base metal surface. As the electrode potential of the noble metal is lower, they protect the base metal.

  e.g. Application of Cu, Sn, Ni, Cr, Ag coating on iron surface.

- Cathodic coating can provide complete protection to the base metal till the coat layer is intact. But the moment this layer is broken, the base metal get exposed. Since the electrode potential of base metal is higher than that of the coated metal, a galvanic cell is set up where anode is small (exposed base metal) and cathode is larger (coated metal). This gives rise to severe corrosion of base metal.

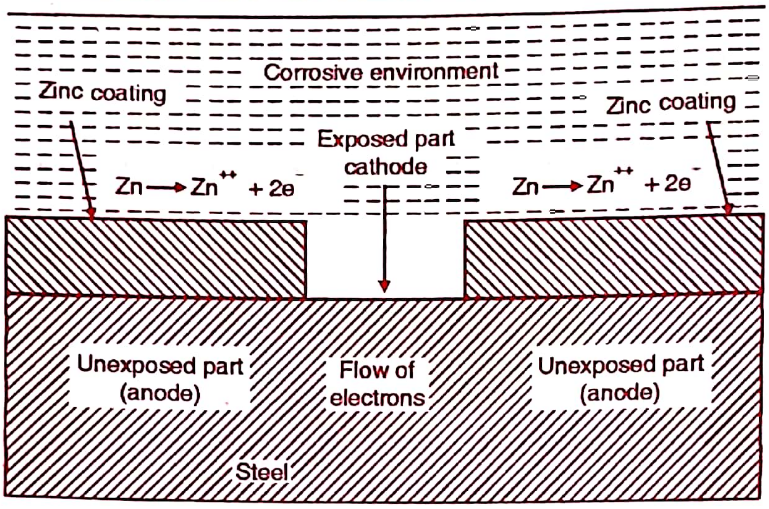


Fig. 2.6.3 : Poor protection of base metal due to cathodic coating (Schematic representation)

- *Example : Tin coating on iron surface.* In this case, tin coating can provide protection to iron surface *only till the coated layer is without any breaks.* If, due to any external factors, the coated layer is punctured, immediately there is formation of galvanic cell where *base metal (iron) acts as an anode* and the coated metal (tin) acts as a cathode. Since, cuts are normally minute, *the anode is small and cathode is large.* Thus, in corroding environment, the rate of corrosion is very high. This continues, till coated layer is repaired to be intact again.

2.6.1(A) Comparison between Anodic and Cathodic Coatings

Sr. No.	Anodic coating	Cathodic coating
1.	This type of coatings protect base metal "sacrificially".	This type of coatings protect the base metal because of **high corrosion resistance and noble behaviour**.
2.	The coating metal is at lower electrode potential than base metal.	The coating metal is at higher electrode potential than base metal.
3.	Corrosion of base metal does not enhance even on breaking "anodic coating", as it heals its film.	Corrosion of base metal enhances, if there is small cut / break in coating.
4.	E.g. Galvanizing, i.e. Zn coating on iron / steel.	E.g. Tinning, i.e. Tin coating on iron / steel / copper / brass.

2.7 Corrosion in Electronic Devices

Electronic corrosion is "the deterioration or degradation of electronic components and circuits due to corrosion." This corrosion occurs due to oxidation or moisture related reactions or chemical corrosion.

Occurrence

In electronic devices if different metals are in contact or electrically connected, they form galvanic cells due to difference in electrode potentials. The galvanic cell results in flow of electrons between the metals in contact, causing corrosion.

Corrosion control

i) Remove battery from device.

ii) Apply white vinegar or lemon juice in slots where acidic residue is spread due to leakage of battery.

Protection of devices

i) Use anti tarnish vapour capsules, which are of non-ferrous alloys.

ii) Rust prevention vapour capsules can be used.

Important Terms and Definitions

- Corrosion is nothing but the *deterioration* of a substance due to its reaction with its environment
- Corrosion is also known as weathering of metals or weeping of metals.
- Such weathering is exhibited by timber, wood, concrete etc. Even leading of glass or cracking of plastics are examples of 'corrosion'
- Thus corrosion can also be defined as "any process causing deterioration or destruction of any material is known as *corrosion*."
- The potential difference between the electrode and its ionic solution at equilibrium at a given temperature is called as *single electrode potential (E).*
- *Oxidation potential* can be defined as, "the potential developed between an electrode and its ions in the solution due to *oxidation reactions* at equilibrium at given temperature (E_{oxd})".

  a) Reduction potential can be defined as, "the potential developed between an electrode and its ions in the solution due to reduction reactions at equilibrium at given temperature (ERed)".

  b) Standard electrode potential can be defined as, "the potential difference between an electrode (element) and its ions in solution at 25°C (298 K) when concentration of all ions are unit molar (E°)".

  There are two types of standard electrode potentials,

  (i) Standard oxidation potential

  (ii) Standard reduction potential.
- Chemical/Atmospheric or dry corrosion occurs mainly by, *direct attack* of atmospheric gases such as O_2, CO_2, H_2S, *halogens*, SO_2 etc. on the surface of metals, thereby forming corresponding compounds such as *oxides, carbonates, sulphides, halides or sulphates.* The action of some *organic* or *anhydrous inorganic liquids, or melt of metals* also cause this type of corrosion.
- Electrochemical or Wet corrosion : When metal surface is in immediate contact of *aqueous acidic/alkaline/neutral/electrolytic solutions*, the short circuited galvanic cells get set all along the surface of metal. This gives rise to corrosion which proceeds by electrochemical principles.
- Differential aeration corrosion is due to the *electrochemical attack* on the metal surface, exposed to an electrolyte *of varying concentrations* or *of varying aeration.* This may be the result of local difference in metal ion concentration caused by,

  (i) local difference in temperature

  (ii) inadequate agitation
- Slow diffusion of metal ions, produced by corrosion.
- Polarization : The phenomenon which alters/ makes the cathode to be less cathodic (or more anodic) and that of the anode to be less anodic (or more cathodic) is called polarization of electrodes.

Note : Polarization at the electrodes is due to : (i) concentration changes in the electrode region, (ii) overvoltage or (iii) presence of surface films on the electrodes.

Corrosion control

i) Remove battery from device.

ii) Apply white vinegar or lemon juice in slots where acidic residue is spread due to leakage of battery.

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Note : Polarization at the electrodes is due to : (i) concentration changes in the electrode region, (ii) overvoltage or (iii) presence of surface films on the electrodes.

- "The difference between the potential of the electrode when the gas evolution was actually observed and the theoretical reversible value of the same solution was called the *overvoltage or overpotential*".

Note : Overvoltage may occur at the anode as well as the cathode.

- Cathodic protection involves reversal of the flow of current between the two dissimilar metals, under corroding environment thereby reversing the action of the metals in contact.

Note : This is achieved by applying the external circuit and forcing the anodic metal to behave as a cathode.

- Anodic protection involves suppression of anodic reaction by adjusting the potential of the more reactive metal, i.e. making metal passive in the working environment.

Review Questions

Q. 1 a) Describe the various factors which influence the rate of corrosion.

b) Give an account of the different methods used for the application of metallic coatings for prevention of corrosion.

Q. 2 a) Discuss the corrosion caused due to the formation of concentration cells.

b) Explain following methods for corrosion control.
   i) Design and protection
   ii) Cathodic protection.

Q. 3 Write a short note on the following :
i) Concentration cell corrosion
ii) Galvanic corrosion

Q. 4 What is corrosion ? Discuss the corrosion caused due to the combination of metals of different electrode potentials.

Q. 5 Mention the various methods of metallic coatings and explain any two of them.

Q. 6 What is corrosion ? Discuss the corrosion caused due to the formation of galvanic cells.

Q. 7 Mention the important methods of controlling corrosion and explain the method of cathodic protection.

Q. 8 What is corrosion ? Explain the mechanism of electrochemical corrosion.

Q. 9 Write informative notes on :
i) Electroplating.
ii) Integranular corrosion
iii) Cathodic protection

Q. 10 a) How do the metals undergo corrosion ?

b) Explain, how corrosion can be prevented by the following methods :
   i) Proper design
   ii) By using alloys

Q. 11 a) How do the following factors influence the corrosion rate :
   i) Position of metal in galvanic series
   ii) Oxygen
   iii) Temperature

b) How can you prevent the corrosion of buried pipelines ?

c) Write a note on electroplating.

Q. 12 Describe any two methods of metallic coating for corrosion control.

Q. 13 What are the factors responsible for influencing corrosion.

Q. 14 Discuss the principle of electro-plating.

Q. 15 a) What is corrosion ? Explain the dry/chemical corrosion ?

b) How is the rate of corrosion influenced by the following factors :

i) Temperature

ii) Nature of corrosion products

Q. 16 What is corrosion ? Discuss the corrosion due to differential aeration.

Q. 17 Discuss electro-chemical theory of corrosion taking suitable examples with neat sketch.

Q. 18 Distinguish between anodic and cathodic coatings.

□□□

3

Alloys

Syllabus

A) Purpose of making alloys.

B) i) Gibbs Phase rule – Statement, Terms involved with examples.

ii) Reduced phase rule, Two-component system (Pb-Ag) & Numerical. iii) Merits and Limitations of Phase rule.

3.1 Introduction

- Metals possess many useful properties, such as high malleability, ductility, lustre, good electrical conductivity being a few to mention. But, in nature metals are not available in pure state.
- When metals are extracted from their natural sources. i.e. minerals or ores, some impurities are carried along with the pure metals. Hence, to get pure metal, further purification has to be done, by various different methods. But after all this processing, the pure metal obtained from its ore, *loses some vital characteristics* and becomes practically less useful for engineering purposes.
- Some of such characteristics are, its *tensile strength, corrosion resistance and toughness.* The pure metals are very soft, highly chemically reactive, highly malleable and ductile. Thus changes in these vital properties, *reduce shock and wear resistance* of metals. The high chemical reactivity makes pure metal susceptible to corrosion.
- The properties of pure metals can be improved by alloying the pure metal with another suitable metal/non-metal, For example, Pure iron can be alloyed to get steel, which shows the desired properties such as, toughness, *high corrosion resistance etc.* Here, steel is an alloy of iron with carbon (non-metal), chromium/manganese (metals) etc.

3.1.1 Alloy

- An alloy is a solid mixture of two or more metals or non-metals. Alloy must have necessarily,
  (i) at least one metal (base metal)
  (ii) at least one additional metal or non-metal.
- The properties of given metal (base metal) can be improved by alloying it with other metals or elements like *carbon, phosphorus* etc.
- When two or more metals are mixed in their molten state and when this mixture is cooled, the two metals remain in intimate mixture without separation, thus forming a solid mixture. This solid homogeneous mixture of two metals is called as alloy. Thus, an *alloy is a substance/material formed by solidification of metallic solution of two or more metals/elements.*
- Alloy can also be defined as a solid solution where the solutes are the alloying elements whereas the solvent is the element in excess proportion (base or main metal).
- The *homogeneous mixture* of two or more metals must retain metallic characteristics and it also must improve the properties of individual elements.

3.2 Purpose of Making Alloys

- Metals are used as a basic material in making various machines, used in industries or household articles or in other areas like making ships, railways, bridges, buildings etc.
- During metallurgical processes involved in extraction of pure metal from its ores, the most important characteristics of metal are been lost/reduced, as discussed above. This affects the performance of metals during operation under given service conditions in engineering uses.
- The undesirable changes in the malleability, ductility, tensile strength, elastic limits, hardness have to be improved to make the metal suitable for its uses, which are affected by mixing the metals with other suitable elements.
- Thus alloy formation, basically helps in getting the desired performance in the given service conditions economically.
- The following properties of metals are generally modified/improved by alloying the metal, i.e. the purpose of alloying the metal is to improve,

  (i) Hardness

  (ii) Tensile strength

  (iii) Corrosion resistance

  (iv) Castability

  (v) Colours

  While to decrease,

  (vi) Melting point

  (vii) Malleability and ductility

  (viii) Chemical reactivity.
- The Table 3.2.1 shows different examples indicating the improvements in the characteristics of main element on alloying with others.

Table 3.2.1 : Improvements in characteristics

Sr. No	Characteristic	Main Metal	Alloying Elements	Modification in Properties of Main Metal
1)	Hardness	Pure Lead	Arsenic (0.5%)	*Hardness* of lead *improves* and it is used to make bullets.
		Pure Gold	Copper	Ornaments of gold are prepared as *hardness of gold improves.*
		Pure Iron	Carbon (upto 1.5%)	To make steels with greater hardness.
		Pure Copper Pure Copper	Tin Zinc	Alloy is harder than pure copper.
2)	Tensile strength	Pure Iron	Carbon (1%)	Ten times increase in tensile strength of iron
3)	Corrosion resistance	Pure Iron	Chromium, Nickel	The alloy (stainless steel) *does not get corroded,* not only by moisture but even in acids, whereas pure iron gets corroded easily by the attack of atmospheric gases, moisture etc.

Sr. No	Characteristic	Main Metal	Alloying Elements	Modification in Properties of Main Metal
4)	Castability	Pure Lead	Tin, antimony	Castability of this alloy improves and hence it is used in making *'printing type'*.
5)	Colours	Silver *(White)*	Gold *(yellow)*	The alloy is *purple* coloured.
		Silver *(White)*	Tin *(white)*	The alloy is *pink* coloured
		Copper *(Red)*	Zinc *(silvery white)*	The alloy is *yellow* coloured.
		Aluminium *(Silvery white)*	Zinc *(silvery white)*	The alloy is *golden yellow* in colour.
6)	Melting point	Pure Iron M.P. = 1539°C	Carbon (2%)	M.P. of alloy *is decreased* to *1130 °C*
		(Bi) Bismuth M.P. = 271°C	Cd (321°C) Pb (327°C) Sn (232°C)	The alloy (wood's metal) has M.P. of only 71°C, which is very low as compared to alloying elements.
7)	Malleability and ductility	Copper Gold	Zinc Copper	The alloy (brass) is less ductile as compared to copper. The malleability of gold is reduced.
8)	Chemical activity	Iron	Chromium Nickel	The alloy (stainless steel) has very low reactivity as compared to pure iron.

Thus, from above table, the purpose of making alloys in understood clearly, as each example indicates the modification/improvements in specific property (drawback) of pure metal. *The alloying helps in enhancing the utility of metals for engineering purposes.*

3.3 Gibb's Phase Rule : Introduction

Q.	Define Gibb's Phase Rule.	Dec. 12, Dec. 13, May 15, Dec. 15, 2 Marks
Q.	What is the mathematical form of the Gibb's phase rule equation ?	May 17, 3 Marks

- Phase rule is an important generalization given by Willard Gibbs (1874) which deals with the behaviour of heterogeneous systems in the state of equilibria.
- In general, with the application of phase rule, it has been possible to *predict* qualitatively (by means of a diagram) the *effect of* changing *temperature, pressure* and *concentration* on a heterogeneous system in equilibrium. Such a diagram is known as *'phase diagram.'*
- This heterogeneous system containing two or more different phases which exist in equilibrium with each other is studied with the help of generalization called *phase rule.* This rule was deduced on the basis of principles of thermodynamic by an American physicist Willard Gibbs to explain the equilibria existing in heterogeneous system.

Phase Rule Equation / Statement of Phase Rule

Gibb's Phase rule may be stated as, "provided equilibrium between any number of phases is not influenced by gravitational, electric or magnetic forces or by surface action, but only by temperature, pressure and concentration, then the number of degrees of freedom (F) of the system is related to the number of components (C) and phases (P) by the phase rule equation.

$$F = C - P + 2$$

For any system at equilibrium at definite temperature and pressure". This rule does not have an exception, if applied properly by maintaining the variables at a fixed levels.

3.3.1 Explanation of Phase Rule

- Let us consider a *heterogeneous system in equilibrium* consisting of 'C' components distributed in 'P' phases. As has been already defined, the number of degrees of freedom of a system in equilibrium is that number of variable factors (such as temperature, pressure and composition) that must be arbitrarily fixed to define the system completely.
- Obviously, the number of such variables is given by the total number of variables of the system minus the number of variables which are defined automatically by virtue of the system being in equilibrium.
- When a system is in equilibrium, there can be only one temperature and one pressure hence, the total of these variables is two only.
- However, the number of concentration (or composition) variables can be more. In order to define the composition of each phase, it is necessary to specify only (C – 1) composition variables because the composition of the remaining component can be obtained by difference.
- Since there are P phases, the total number of composition or concentration variables will be P (C – 1). On adding the temperature and pressure variables, the total number of variables of the system are P (C – 1) + 2.
- On the basis of thermodynamic considerations, when a heterogeneous system is in equilibrium, at a constant temperature and pressure, the chemical potential, μ of a given component must be same in every phase.
- Thus, if there is one component in three phases (say α, β and γ) and one of these (say α) is referred to as standard phases, then, this fact must be expressed in the form of the following two equations.

$$\mu_\alpha = \mu_\beta$$

$$\mu_\alpha = \mu_\gamma$$

- Thus, for each component in equilibrium in 3 phases, 2 equations are possible. Hence for each component in 'P' phase, (P – 1) equations can be written. If there are 'C' component the number of equations or variables possible from the conditions of equilibrium are C (P – 1).
- Since chemical potential is a function of temperature, pressure and concentration, each equation must represent one variable.
- Hence, the number of possible variables of degree of freedom can be given as,

$$F = \{P(C-1) + 2\} - C(P-1)\}$$

$$\therefore \quad F = C - P + 2$$

3.3.2 Terms Involved in Gibb's Phase Rule

Q. Explain the meaning of each one of the terms involved in Gibb's Phase Rule. **May 17, May 19, 2 Marks**

The following terms are involved in phase rule,

(i) Phase
(ii) Components
(iii) Degrees of Freedom (variance)

Let us discuss each term with examples.

3.3.2(A) Phase

Q. Explain terms phase by giving appropriate examples. **May 15, Dec. 16, May 18, Dec. 18, 1 Mark**

Definition :

A phase is defined as *any homogeneous, physically distinct and mechanically separable portion of a system, which is separated from other such parts of the system by definite boundary surfaces.*

Examples

1. In water system, at freezing point of water, an equilibrium exists where ice, water and water vapours are the three phases, each of which is physically distinct and homogeneous, and with definite boundaries between ice, water and water vapours, as,

$$\text{Ice}_{(S)} \rightleftharpoons \text{Water}_{(L)} \rightleftharpoons \text{Water Vapour}_{(G)}$$

2. *All gases mix freely to form homogeneous mixtures.* Therefore, any mixture of gases, say O_2 and N_2 and H_2 forms *one phase* only.
3. Two completely *miscible liquids* yield an uniform solution. Thus, a solution of alcohol and water is a *one phase* system.
4. A mixture of *two non-miscible liquids* on standing forms two separate layers. Thus, a mixture of an oil and water constitutes a *two phases* system.
5. An *aqueous solution* of a solid substances like salt (NaCl) or sugar is uniform throughout. Therefore, it is a *one phase* system.
6. Each solid substance makes a separate phase except in the case of solid solutions.
   e.g. Allotropic forms of Sulphur or Carbon, though all exist together, but are all separate phases.
7. Equilibriums given below,

(i)
$$\underset{\text{(Solid)}}{CaCO_3} \rightleftharpoons \underset{\text{(Solid)}}{CaO} + \underset{\text{(Gas)}}{CO_2}\uparrow \left[\begin{array}{c}\text{Contain}\\ \text{two phases}\\ \text{solid and gaseous}\end{array}\right]$$

(ii)
$$\underset{\text{(Solid)}}{Fe} + \underset{\text{(Gaseous)}}{H_2O} \rightleftharpoons \underset{\text{(Solid)}}{FeO} + \underset{\text{(Gas)}}{H_2}\uparrow$$

(Two phases exist in equilibrium)

3.3.2(B) Components

Q. Explain term component by giving appropriate examples. **May 15, Dec. 16, Dec. 18, 1 Mark**

Q. State the number of component for the following equilibrium :

(i) $H_2O_{(S)} \rightleftharpoons H_2O_{(l)} \rightleftharpoons H_2O_{(g)}$

(ii) Mixture of rhombic and monoclinic-sulphur. **May 16, Dec. 17, 2 Marks**

Definition

The term component is defined as, "the smallest number of independently variable constituents taking part in the state of equilibrium by means of which the composition of each phase can be expressed directly or in the form of chemical equation".

Examples

1. In water system, we have three phases, i.e. ice (Solid), water (Liquid) and water vapour (Gaseous) in equilibrium. Each of these phases are different physical forms of the same chemical substance, i.e. H_2O. Hence, system is regarded *one component* system.

Phase : $Ice_{(S)} \rightleftharpoons Water_{(L)} \rightleftharpoons Water\ Vapour_{(G)}$

Component : H_2O H_2O H_2O

2. In *sulphur system*, there are four phases, i.e. *rhombic* sulphur, *monoclinic* sulphur, *liquid* sulphur and sulphur *vapour*. The composition of all four phases can be expressed by one chemical individual sulphur (S). Hence, sulphur system is regarded as *one component* system.
3. When calcium carbonate is heated in a closed vessel, the following reaction takes place.

$$CaCO_{3(S)} \overset{\Delta}{\rightleftharpoons} CaO_{(S)} + CO_{2(G)}$$

From the above reaction, it comes to know that, there are three phases $CaCO_{3(S)}$, $CaO_{(S)}$ and $CO_{2(G)}$. Thus, the decomposition of $CaCO_3$ gives $CaO_{(S)}$ and $CO_{2(G)}$, i.e. system is *two component* system. Although this system has three different constituents, it is considered as *two component* system because *the composition of each of the above phase can be expressed in terms of any two of the three constituents present.*

This can be understood from following illustration,

If only $CaCO_3$ and CaO are considered as components, then composition of each can be given as :

Phase : $CaCO_3 = CaCO_3 + 0CaO$ (Zero)

Phase : $CaO = 0CaCO_3 + CaO$ (Zero)

Phase : $CO_2 = CaCO_3 - CaO$

Thus it is a two component system.

4. In the equilibrium, for reaction between iron metal and steam,

$$Fe_{(S)} + H_2O_{(G)} \rightleftharpoons FeO_{(S)} + H_{2(G)}$$

the composition of each phase can be expressed in terms of the components Fe, H_2O and H_2. Hence, it is a *three component* system.

5. In the *dissociation of* NH_4Cl *in a closed vessel*, which can be represented as,

$$\underset{(Solid)}{NH_4Cl} \rightleftharpoons \underset{(Gas)}{NH_4Cl} \rightleftharpoons \underset{(Gas)}{NH_3} + \underset{(Gas)}{HCl}$$

In this case if proportions of NH_3 and HCl are equivalent, then the system is one component system; this is because the composition of both can be expressed in terms of NH_4Cl alone.

But if NH_3 or HCl is in excess, the system becomes a two component system.

6. Saturated solution of NaCl in water, contains solid salt, salt solution and water vapour. The chemical composition of all the three phases can be expressed in term of NaCl and H_2O. Hence, it is a *two component* system.
7. Dissociation reaction, as,

$$\underset{(Solid)}{CuSO_4 \cdot 5H_2O} \rightleftharpoons \underset{(Solid)}{CuSO_4 \cdot 3H_2O} + \underset{(Gas)}{2H_2O}$$

[Two component system : $CuSO_4$ and H_2O].

3.3.2(C) Degree of Freedom (Variance)

Q. Explain term degree of freedom by giving appropriate examples.

Dec. 12, May 13, May 14, May 15, Dec. 16, Dec. 18, 1 Mark

Q. Using phase rule, find the number of degrees of freedom (F) for the following systems ;

(i) $Ice_{(s)} \rightleftharpoons Water_{(l)} \rightleftharpoons Water\ vapour_{(g)}$

(ii) Water $\rightleftharpoons$ Water vapour

Dec. 15, 2 Marks

Definition

Term degree of freedom is defined as, "the minimum number of independently variable factors such as temperature, pressure and composition of the phases which must be arbitrarily specified in order to represent perfectly the condition of a system".

Examples

1. In case of *water system :*

   (a) If all the three phases are in equilibrium, then no condition need to be specified because the three phases can be in equilibrium only at particular *temperature and pressure,*

   $$\text{Ice}_{(S)} \rightleftharpoons \text{Water}_{(L)} \rightleftharpoons \text{Water vapour}_{(G)}$$

   The system is *no degree of freedom or invariant or zero variant or non-variant.*

   (b) If condition like temperature or pressure in altered, three phases will not remain in equilibrium and one of the phase disappears.

   For the following system :

   $$\text{Water}_{(L)} \rightleftharpoons \text{Water vapour}_{(G)}$$

   We must state *either the temperature or pressure* to define it completely. Hence, the degree of freedom is *one* or system *univariant.*

   (c) For a system consisting of water in vapour phase only we must state the values of both, *the temperature and pressure* in order to describe the system completely. Hence, the system has *two* degree of freedom or system is *bivariant.*

2. For mixture of gases, degree of freedom is two because a system containing a mixture of two or more gases e.g. $N_2 + H_2$ is completely defined when its temperature and pressure are specified. *If pressure and temperature are specified, the composition, i.e. third variable could be automatically definite.* Since, it is necessary to specify two variable to define a system completely. Hence, the system is a *bivariant.*

3. A system containing saturated solution of sodium chloride in equilibrium with a solid sodium chloride and water vapour is

   $$\underset{(Solid)}{\text{NaCl}} \rightleftharpoons \underset{(Solution)}{\text{NaCl} - \text{Water}} \rightleftharpoons \underset{(Gas)}{\text{Water vapour}}$$

   completely defined if the *temperature* is specified. Hence, the system has *one* degree of freedom. The other two variables, i.e. composition of NaCl solution and vapour pressure have definite value at a fixed temperature.

3.3.3 Reduced or Condensed Phase Rule

- When a single phase is present in a *two component system,* then the degree of freedom (F) is represented by following equations;

$$F = C - P + 2$$
$$F = 2 - 1 + 2$$
$$F = 3$$

- From the values of F (F = 3) we can say that, three variables must be specified in order to describe the condition of phase, i.e. *in addition to temperature and pressure the concentration of one of the component has to be given.*

3.4 Two Component Systems (Pb-Ag)

General characteristics of two-component systems

(1) The maximum number of phases in a two-component system will be four.

$$P = C - F + 2 = 2 - 0 + 2 = 4$$

(Maximum number of phases exist when degrees of freedom = 0. *Negative degree of freedom cannot exist*).

(2) The maximum number of degrees of freedom in a two-component system will be three (i.e. when the system exists as a single phase)

$$F = C - P + 2 = 2 - 1 + 2 = 3$$

(3) The system will have three variables namely, temperature, pressure and concentration.

(4) The composition of all the individual phases of the system can be expressed by means of *not less than two components.*

(5) For constructing a phase diagram of a two-component system, a three dimensional space model is required using the three variables (viz., temperature, pressure and concentration) as its coordinates.

Phase rule for two component alloy systems

- In two-component system, when p = 2, degree of freedom (F) has the highest value, i.e., 3.

$$F = C - P + 2 = 2 - 1 + 2 = 3$$

- Consequently, three variables – temperature, pressure and concentration of one of the two components must be specified in order to describe the system completely.
- Since the maximum number of degrees of freedom in a two-component system is three, the phase behaviour of a binary system may be represented by a three-dimensional diagram of pressure, temperature and composition or space models, which cannot be conveniently shown on paper.
- A solid-liquid equilibrium of an alloy has practically no gas phase and the effect of pressure is small on this type of equilibrium. Therefore, experiments are, usually conducted under atmospheric pressure.
- Thus, keeping the pressure constant or a system in which vapour phase is not considered, is known as condensed system.
- Since pressure is kept constant (at 1 atmosphere).
- It will reduce the degrees of freedom of the system by one, and for such a system, the phase rule becomes :

$$F = C - P + 1$$

- This is known as the *reduced phase rule* having two variables, namely, *temperature and concentration* (or composition) of the constituents.

3.5 Lead Silver System

6m

Q. Draw the phase diagram of an Ag-Pb system with proper labelling. **May 15, Dec. 17, 3 Marks**

Q. Draw and explain phase diagram of Pb-Ag system. **May 19, 4 Marks**

- This system has two component and four phases. The phases are :

(1) Solid silver
(2) Solid lead
(3) Solution of molten silver and lead and
(4) Vapour

But the boiling points of silver and lead being considerably high, the vapour phase is practically absent.

- Since the pressure has nearly no effect on equilibrium so the system can be conveniently represented by a *temperature-concentration diagram* (see Fig. 3.5.1) *at a constant and one variable pressure which is neglected,* the condensed form of the phase rule :

$$F - C - P + 1 = 2 - P + 1 = 3 - P$$

will be applicable.

- When system containing two phases and two components like solid and liquid, then solid-liquid equilibrium has practically *no gas phase* and the effect of pressure is very small that is negligible. Then, it is necessary to take into account the remaining variables, viz. temperature and concentration. *Such a solid-liquid system with the gas phase is absent is called a condensed system.*
- The experimental measurements of temperature and concentration in condensed systems are usually carried out under atmospheric pressure.
- Since, the degree of freedom in such case is reduced by one, therefore, it can be also termed as *reduced phase rule* and represented by the equation.

$$F = C - P + 1$$

- The reduced phase rule is more convenient to apply to solid-liquid two components condensed system. Example Pb - Sb, Ag - Pb or Zn - Cd system.
- The complete Temperature - Concentration (T-C Phase) phase diagram of the system Silver - Lead (Ag - Pb) is shown in Fig. 3.5.1.

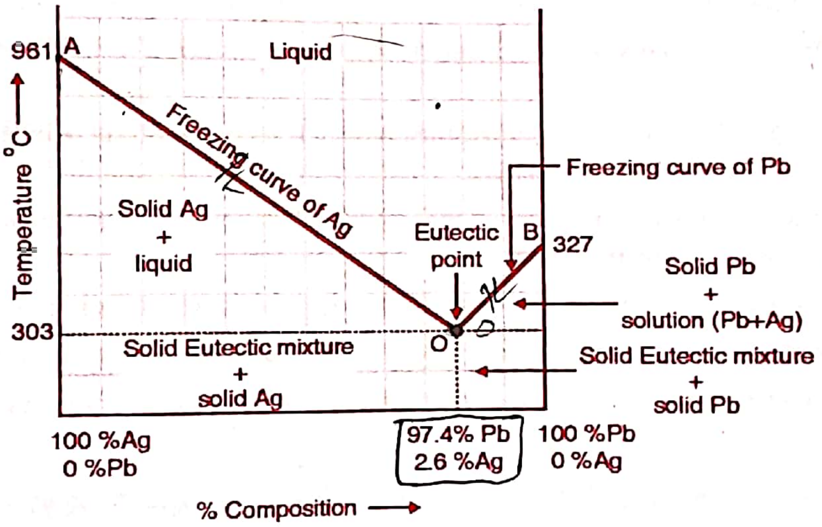


Fig. 3.5.1 : The phase diagram of Pb- Ag system

- In the phase diagram shown in Fig. 3.5.1 of Pb-Ag system, following salient features are observed.

(i) The curve AO (Freezing curve of Ag)
(ii) The curve BO (Freezing curve of Pb)
(iii) The eutectic point 'O'
(iv) The Area AOB

(1) Curve AO (Freezing curve of Ag)

- It shows the effect on freezing point of Ag on addition of lead in small quantities.
- The curve starts from A (961°C) the melting point of Ag, where pure Ag coexists as solid and liquid (vapour being neglected).

- This curve, indicates that the melting point of Ag falls gradually on adding Pb, along AO, till the lowest point O (303°C) is reached, *where the solution gets saturated with respect to lead.* At O, no more lead can go in solution and consequently, the melting point does not fall any further, and if any lead is added, *it separates as the solid phase.*
- Along this curve, solid Ag and solution (vapour being negligible) coexist and hence, according to reduced phase rule equation :

$$F = 3 - P = 3 - 2 = 1$$

i.e. the system is univariant. The point O (303°C) corresponds to a *fixed composition of 2.6% Ag and 97.4% Pb and is known as eutectic composition.* On cooling the whole mass crystallizes out as such.

(2) Curve BO (Freezing curve of Pb)

- It represents the effect on freezing point of Pb on gradual addition of small amounts of Ag to it. Point B is the melting point of pure lead *(327 °C).*
- Along BO, the melting point gradually falls on the addition of Ag, till lowest point O is reached.
- At this point the solution gets saturated with respect to Ag and the melting point of lead does not fall any more.
- On cooling the whole mass (having eutectic composition) crystallizes out. The system is univariant like AO.

(3) Point O (Eutectic point) [Eutechic mixture).

3M
- The two curves AO and BO meet at O, where three phases-solid Ag, solid Pb and their solution coexist and according to condensed phase rule, the system will be invariant $(F = 3 - P = 3 - 3 = 0)$
- The point O *(303 °C)* represents a fixed composition of *Ag = 2.6 % : Pb = 97.4 % and* is called eutectic composition temperature.
- At the eutectic composition point, the temperature remain constant, until the whole of the melt solidifies in block to become solid of eutectic composition.
- However, further cooling results in the simultaneous crystallization of a mixture of Ag and Pb in relative amounts corresponding to eutectic point O.
- Below the temperature line of the eutectic temperature, we have two regions in the diagram viz.
  (i) Region marked as *eutectic + solid Ag,* in which crystalline silver and solid eutectic are stables, and
  (ii) Region marked *eutectic + Pb,* in which crystalline lead and solid eutectic are stable.

(4) Area AOB

- It represents solution of Pb-Ag. If a sample of lead containing *less than 2.6 %* Ag is taken, at an arbitrary point on curve. On allowing the mass to cool, the temperature gradually falls without any change in composition till this point is reached on the curve BO (point may be 'P').
- On lowering the temperature, lead begins to separate out and the composition varies along PO till point O is reached.
- On further cooling the whole mass solidifies in block to the eutectic composition *(2.6 % Ag : 97.4 % Pb).*

3.6 Applications of Phase Rule

Q. Discuss the advantages of phase rule. **Dec. 15, May 16, Dec. 16, Dec. 17, May 18, Dec. 18, May 19, 3 Marks**

1. It applies to physical as well as chemical phase reaction.
2. It provides a convenient basis for classification of equilibrium states of systems with the help of *phases, components and degree of freedom.*

3. It applies to microscopic systems.
4. It indicates that different systems having the *same degrees of freedom* behave in a similar fashion.
5. It helps in predicting the behaviour of a system under different conditions of the governing variables.
6. It helps in deciding whether the given number of substances together would exist in equilibrium under a given set of conditions or whether some of them will have to be inter converted or eliminated.
7. Phase rule does not take any cognizance of the nature of the amounts of substances present in the system.

3.7 Limitations / Demerits of Phase Rule

1. Phase rule can be applied for systems in equilibrium only.
2. It is not of much help in case of systems which attain the equilibrium state very slowly.
3. It applies only to a single equilibrium state. It does not indicate the other possible equilibria in the system.
4. Phase rule considers only the number of phases but not their quantities. Even a minute quantity of the phase, when present, accounts towards the number of phases. Hence, care has to be taken in deciding the number of phases existing in the equilibrium state.
5. All the phases of the system must be present under the same conditions of temperature, pressure and gravitational forces.
6. The solid; liquid phases should not be so finely sub-divided as to bring about deviation from their normal values of vapour pressure.

3.8 Numerical based on Phase Rule

Ex. 3.8.1 : Water is kept in a beaker. Using phase Rule, Calculate number of independent variables are required to determine the thermodynamic state of the water in beaker ?

Soln. : In water molecule,

$$\text{Component (C)} = 1$$

And water in beaker us one phase system.

$$\therefore \text{Phase (P)} = 1$$

$$\therefore F = C - P + 2 = 1 - 1 + 2$$

$$\therefore \text{Degrees of freedom} = 2$$

To determine the thermodynamic state of water, two independent variables should be specified, i.e. Pressure and Temperature.

Ex. 3.8.2 : Calculate independent variable required to determine thermodynamic state of liquid water in equilibrium with its steam.

Soln. :

According to Gibb's phase rule,

$$F = C - P + 2$$

Here, $\therefore$ Component (C) $= 1$

$$\text{Phases (P)} = 2$$

$$\therefore F = 1 - 2 + 2 = 1$$

Thus to know the thermodynamic state of liquid water in equilibrium

$$H_2O(l) \rightleftharpoons H_2O(g)$$

Any one variable to be specified i.e. either pressure or temperature.

Ex. 3.8.3 : Argon gas is dissolved in water. To know the thermodynamic state of system, how many independent thermodynamic variable need to be specified ? Can we know the state ?

Soln. : According to Gibb's phase Rule,

$$F = C - P + 2$$

In this system,

$$\text{Component (C)} = 2$$

$$\text{Phase (P)} = 1$$

$$\therefore \quad F = 2 - 1 + 2 = 3$$

Hence, in this system, we need three variables are,

(i) Temperature

(ii) Volume

(iii) Chemical potential of argon.

Hence for such a system, from concentration of solution, chemical potential need to be found out, which is beyond slope for a solute i.e. Argon.

Ex. 3.8.4 : The gaseous Argon is in equilibrium with liquid water. How many independent thermodynamic variables can define thermodynamic state of Argon in equilibrium ?

Soln. :

$$Ar_{(g)} \rightleftharpoons H_2O_{(l)}$$

As per Gibb's phase Rule,

$$F = C - P + 2$$

$$\text{Here, } C = 2$$

$$P = 2$$

$$\therefore F = 2 - 2 + 2 = 2$$

Hence two variables need to be specified.

Important Terms and Definitions

- **Alloy** can also be defined as a solid solution where the solutes are the alloying elements whereas the solvent is the element in excess proportion (base or main metal).
- Metals are used as a basic material in making various machines, used in industries or household articles or in other areas like making ships, railways, bridges, buildings etc.
- Gibb's Phase rule may be stated as, "provided equilibrium between any number of phases is not influenced by gravitational, electric or magnetic forces or by surface action, but only by temperature, pressure and concentration, then the number of degrees of freedom (F) of the system is related to the number of components (C) and phases (P) by the phase rule equation.

  $$F = C - P + 2$$

- For any system at equilibrium at definite temperature and pressure". This rule does not have an exception, if applied properly by maintaining the variables at a fixed levels.
- A phase is defined as any homogeneous, physically distinct and mechanically separable portion of a system, which is separated from other such parts of the system by definite boundary surfaces.
- The term component is defined as, "the smallest number of independently variable constituents taking part in the state of equilibrium by means of which the composition of each phase can be expressed directly or in the form of chemical equation".

- Term degree of freedom is defined as, "the minimum number of independently variable factors such as temperature, pressure and composition of the phases which must be arbitrarily specified in order to represent perfectly the condition of a system".

Review Questions

Q.1 State Gibb's phase rule with equation.

Q.2 Explain the term 'condensed' or 'reduced' phase rule.

Q.4 Explain the term 'Degree of Freedom' with examples.

Q.5 What do you understand by the term "Phase" and "Component".

Q.6 State Gibb's phase rule and explain the various terms involved in it with examples.

Q.7 What is phase rule ? Explain the application of phase rule to "One Component" or "Water System".

Q.8 State limitations of phase rule.

Q.9 Explain shape memory effect and give its application.

□□□

4

Introduction to Polymers

Syllabus

A) Macro-molecular science, basic concept of polymers, Chemical bonding in polymers, Classification of Polymers.

B) Properties of Polymers :- i) Molecular weight - Number average molecular weight, Weight average molecular weight, Numerical, ii) Crystallinity - Crystalline and amorphous polymers – Glass transition temperature, iii) Mechanical Properties: Hardness, tensile strength, creep, fatigue, impact resistance (introduction), iv) Electrical properties: dielectric strength, insulation resistance, surface resistivity (Introduction), v) Optical properties: refractive index, transmittance, photoelectric property, colour.

4.1 Introduction

- The compounds formed by large number of small molecules (called monomers) linked together are known as *polymers* [poly = many].
- The polymers are giant molecules with high molecular masses. For example, the monomer ethylene, gets linked with many other ethylene molecules to form polyethylene, or large number of vinyl chloride molecules combine to form polyvinyl chloride.

Monomer and polymer

Thus the single repeating unit is called as *monomer,* and the resultant high molecular weight compound is called as polymer.

High polymers and oligomers

On the basis of this physical property, the polymers with high degree of Polymerisation are known as high polymers while those having comparatively low degree of polymerisation are known as *oligopolymers.*

4.1.1 Macro-Molecular Science

- Macromolecules are high molecular weight substances/materials.
- Macro molecular science is the scientific study of the high molecular materials. It is subfield of material science.
- **Examples :** Biopolymers like nucleic acids, Proteins and carbohydrates, large non polymeric molecules like lipids, nanogels, synthetic fibres, carbon nanotubes etc.

4.1.2 Basic Concepts of Polymers

Polymer Science is a multidisciplinary field/area, e.g. synthetic polymers, biopolymers, etc. It involves fabrication and designing of newer molecules for sustainable and safer environment e.g. Biodegradable polymers.

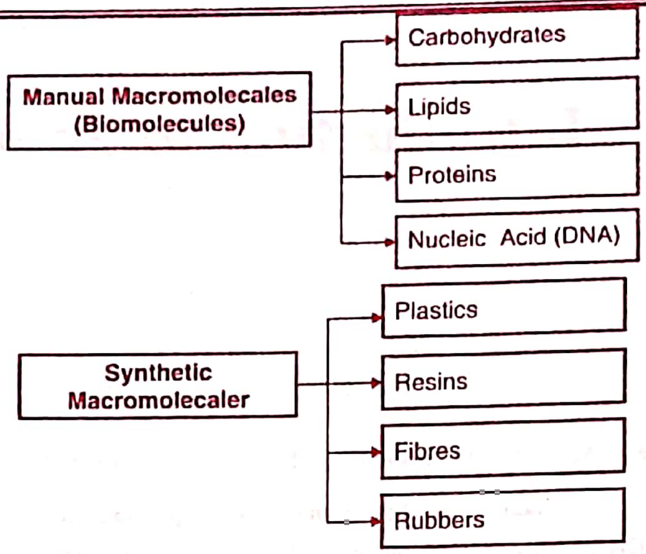


Fig. 4.1.1

4.1.3 Chemical Bonding in Polymers

The polymers are macromolecules formed by combination of smaller molecules called as "monomers".

eg. PVC : Poly Vinyl Chloride (polymer) Vinyl chloride (monomer)

PE : Poly Ethylene (polymer) Ethylene (monomer)

Monomers combine by forming :

(i) Primary bonds i.e. covalent bonds

(ii) Secondary bonds i.e. Van der waals and Hydrogen bonds.

Covalent bonding : By sharing of electrons of S and P shells – mainly to complete the octet.

There are four types of polymers on the basis of molecular forces.

(i) Elastomers. (ii) Fibers (iii) Thermoplastics (iv) Thermosetting polymers

The bonding explains the nature of molecule and reactions of the same. The bonding can be Intra molecular or intermolecular.

4.2 Classification of Polymers

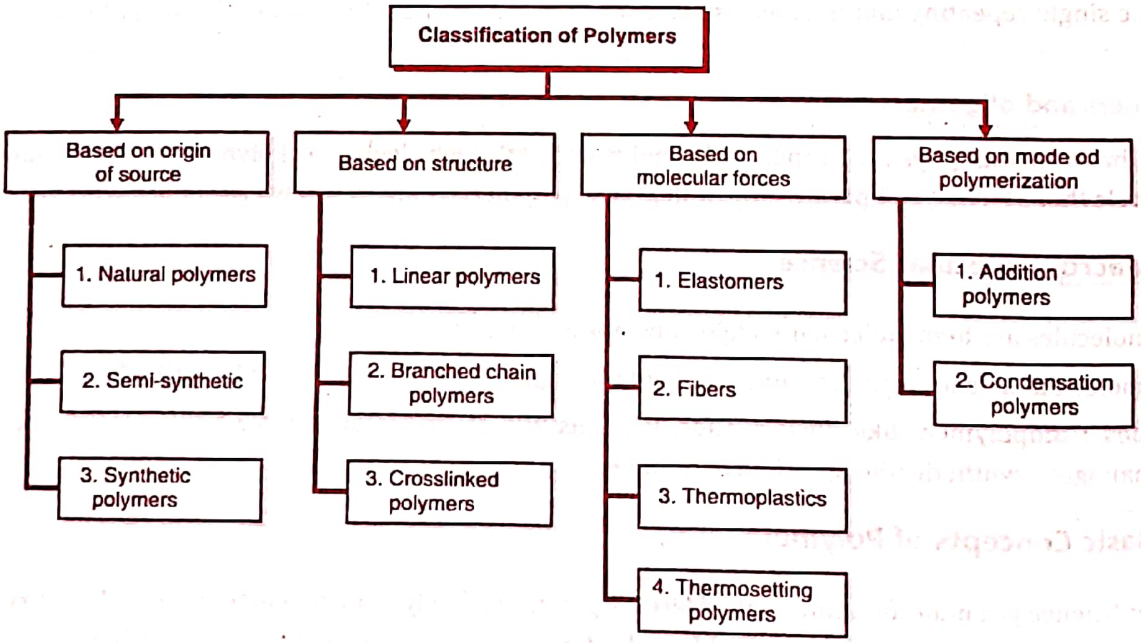


Fig. 4.2.1 : Overall Classification of Polymers

Classification of Polymers

1. By Origin
2. By Monomer
3. By Thermal Response
4. By Mode of Formation
5. By Structure
6. By Application and Physical Properties
7. By Tacticity

4.2.1 Classification of Polymers on the Basis of Origin

1. Natural Polymers

Polymers which are isolated from natural materials are called as natural polymers. E.g. silk, Wool, natural rubber, cellulose, starch, proteins etc.

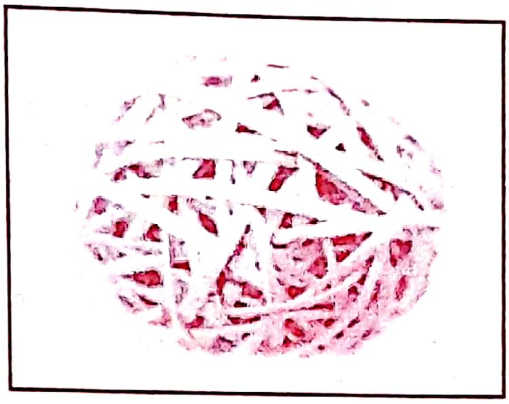
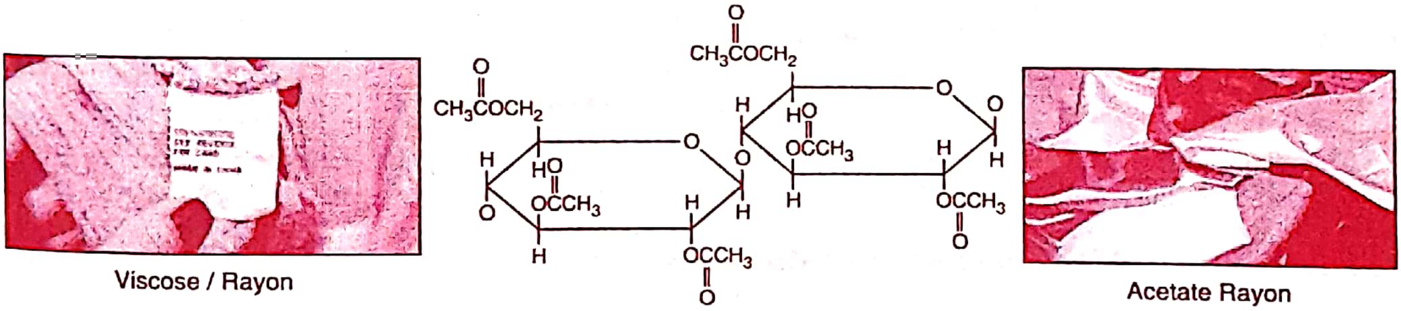


Fig. 4.2.2

2. Semisynthetic Polymers

The polymers obtained by simple chemical treatment of natural polymers to improve their physical properties like lustrous nature, tensile strength are called semisynthetic polymers.

E.g. Cellulose acetate, cellulose nitrate



Viscose / Rayon

Cellulose acetate (acetate rayon)

Acetate Rayon

Fig. 4.2.3

3. Synthetic Polymers

Polymers synthesized in laboratory from low molecular weight compounds, are called as, synthetic polymers. E.g. Nylon, terylene, polyethylene, polystyrene, synthetic rubber, nylon, PVC, bakelite, teflon etc.

Synthetic rubber Teflon tape Polystyren

Fig. 4.2.4

4.2.2 Classification of Polymers on the basis of Monomer

The polymers are also classified on the basis of Monomer

(i) The nature of monomer
(ii) Tacticity
(iii) Chemical nature

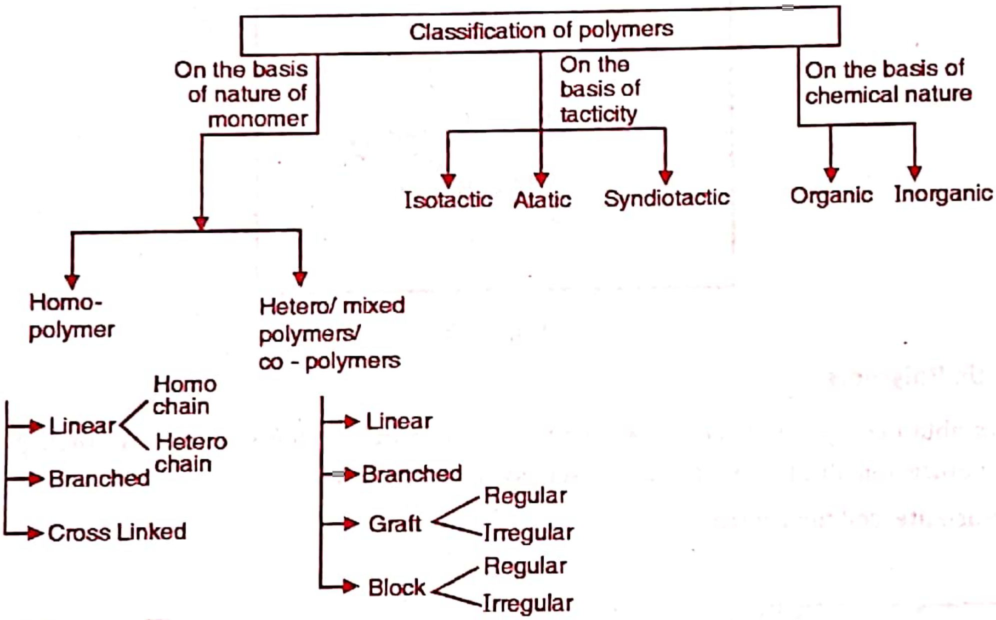


Fig. 4.2.5 : Classification of Polymers

The diversity in structural arrangement of components of monomer units make the polymer, regular or irregular, homo or hetero, linear, branched, or cross linked, block or graft.

4.2.2(A) Homopolymers and Hetero / Mixed / Co-polymers

- **Homopolymers :** The macromolecules formed by identical monomers, are known as *homopolymers* and those with different monomers are known as *mixed polymers or co-polymers.*

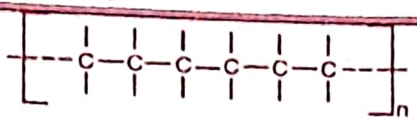
  For Examples, Polythelene, polyvinyl chloride, polyvinyl acetate (PVA), polyvinyl alcohol, polystyrene, polytetrafluoro ethylene (teflon), polypropylene etc.

- **Sub classification (Linear or branched) :** If the main chain of the polymer is of same atoms, it is known as *homo-chain polymers* while, if is of different atoms it is known as *heteropolymer.*

  E.g. $-C-C-C-C-C-$ Homochain polymer

  $-C-O-C-O-C-O-$ Heterochain polymer

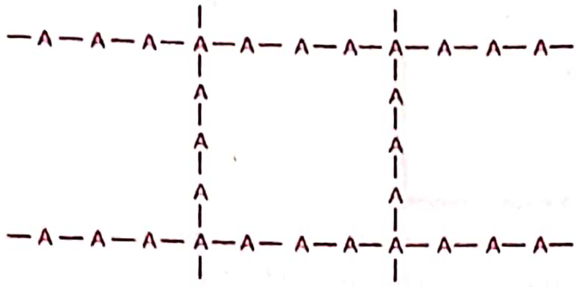
Homopolymers :



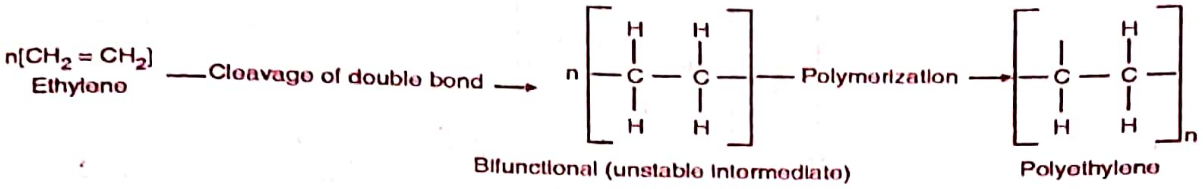
Homopolymer : —A—A—A—A—A—

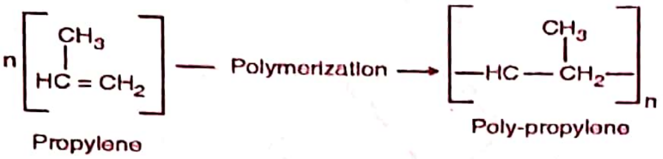
(Linear homopolymer or Homo - chain polymer) : —A—A—A—A—A— A—A—A

(Branched chain homopolymer) :



- **For example :** Polyethylene (PE) / Poly-propylene (PP)





- **Hetero / mixed / Co-polymers :** These are the compounds formed by two *different small molecules.*

  For example in polystyrene butadiene, one molecule of butadiene combines with one molecule of styrene. The product obtained acts as a monomer to get the polymer.

- **Sub classification :** On the basis of arrangement of monomeric units in polymer, these are named as *linear, branched or cross linked* (three dimensional structures).

- **Regular / irregular copolymers :** Co-polymer is named as *regular or irregular* on the basis of arrangement.

  E.g. – A – B – A – B – A – B – A – B – A – Regular

  – A – B – B – A – B – A – A – B – B – Irregular

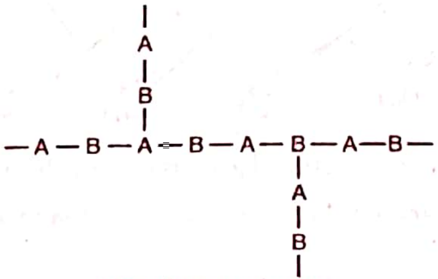
- **Block copolymer :** If co-polymer chain possesses relatively long sequence of like monomers, it is called as *block co-polymer*

- **Graft copolymer :** If co-polymer possesses branched structures in which the monomer segments are not in same sequence on branch and backbone, it is known as *graft co-polymers.*

  A – B – A – B – A – B – A – B ------Co-polymer

—A—B—A—B—A—B—A—B—

(Linear co-polymers)



(Branched co-polymers)

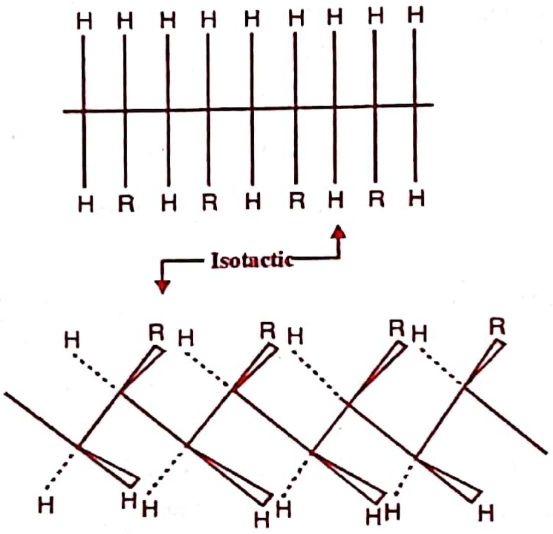
- **Examples of linear high polymers :** Rubber, polyethylene, cellulose, polyvinyl acetate etc. Polyethylene may also have branched chains.

4.2.2(B) Classification on the Basis of Tacticity / Configuration

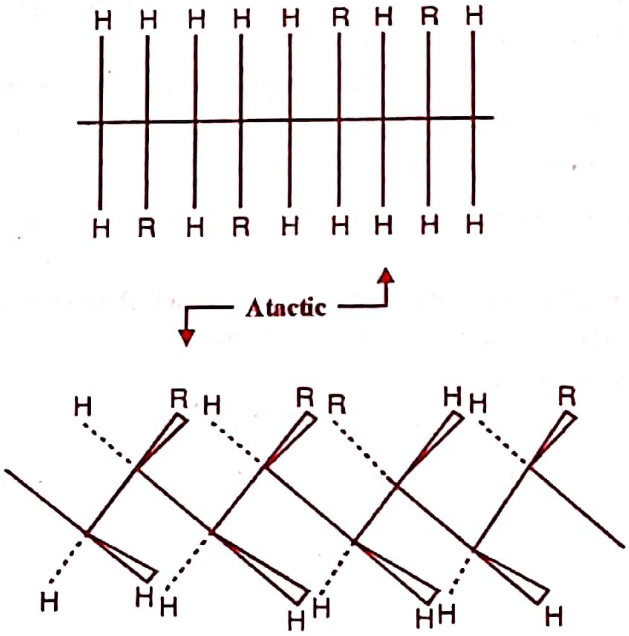
Polymers are also classified on the basis of configuration of macromolecule known as *Tacticity of polymers*.

(a) Isotactic polymers
(b) Atactic polymers
(c) Syndiotactic polymers

(a) Isotactic : In *isotactic*, the head to tail configuration in macromolecule with respect to functional group is iso, i.e. all the functional groups lie on the *same side* of the chain.

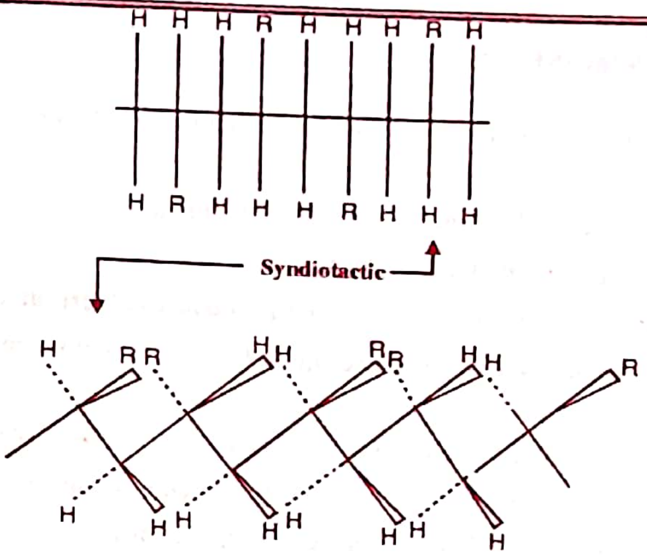


(b) Atactic : In *atactic*, the head to tail configuration is *random* i.e. the functional groups are arranged randomly.



(c) Syndiotactic : In *syndiotactic polymers*, the functional groups occupy the alternating position.

The physical properties of polymers vary, on the basis of the position in which a functional group is attached in macromolecule.



4.2.2(C) Classification based on Chemical Constitution : Organic and Inorganic Polymers

- **Organic polymers :** Generally in organic polymers, *carbon with or without N, S, O forms* the skeleton, e.g. polysaccharides, proteins, DNA, RNA, etc. Man made organic polymers include PVC, PP, PVA, PF, UF, polyesters, polyamides, polyurethanes, synthetic rubbers etc.

Polyethylene :

$$[- - - - H_2C - CH_2 - - - - - -]_n$$

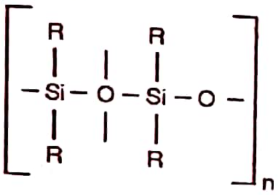
Epoxy polymers :

$$[- - - - O\text{-}R\text{-}O\text{-}CH_2\text{-}CH\ \text{-}OH - CH_2 - - -]_n$$

- **Inorganic polymers :** In inorganic, elements other than carbon form the skeleton.

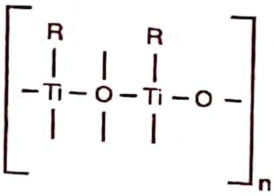
For examples :

Polysiloxanes :



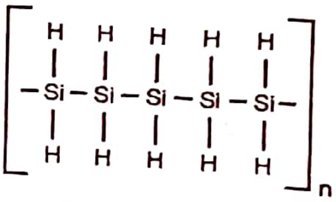
$$\left[-\overset{R}{\underset{R}{Si}} - O - \overset{R}{\underset{R}{Si}} - O - \right]_n$$

Polytitoxanes :

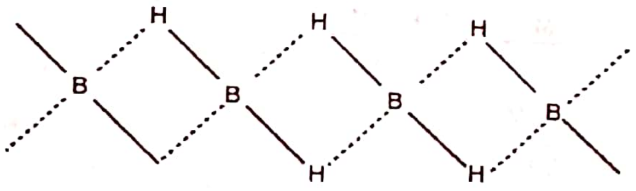


$$\left[-\overset{R}{Ti} - O - \overset{R}{Ti} - O - \right]_n$$

Polysilanes :



$$\left[-\overset{H}{\underset{H}{Si}} - \overset{H}{\underset{H}{Si}} - \overset{H}{\underset{H}{Si}} - \overset{H}{\underset{H}{Si}} - \overset{H}{\underset{H}{Si}} - \right]_n$$



Hydrogen boron

$$[- - - Mg - O - Mg - O - Mg - - -]_n$$

Magnesium oxide polymer

4.3 Properties of Polymers

- The determination of molecular weight of a polymer is highly important because the properties of polymer are totally governed by its molecular weight.
- If polymer is of low molecular weight, then, it is generally softer and vice-versa.

4.3.1 Average Molecular Weight

- In polymerisation reaction, when a monomer faces initiation, it gives rise to a reactive species, i.e. either anion or cation or free radical.
- The type of the reactive species depends upon the path of mechanism.
- In the second step, the propagation or chain elongation occurs.
- This step continues till the monomer molecules are available and also till terminator is applied.
- The final step termination, is random, and therefore the polymer molecule formed from same monomer units also differs in its size, shape and weight.
- Therefore determination of exact molecular weight is not possible in case of polymers.
- Hence, concept of 'average molecular weight' is considered for polymer molecules.
- There are different types of average molecular weights in practice such as,

(i) Number average M.W. ($\bar{M}_n$)

(ii) Weight average M·W ($\bar{M}_w$)

(iii) Viscosity average M·W ($\bar{M}_v$)

4.3.2 Number Average M·W ($\bar{M}_n$)

- To determine $\bar{M}_n$, the following method is used in practice.
- Suppose, a sample contain n polymer molecules out of which say

n_1 molecules have M·W M_1

n_2 molecules have M·W M_2

n_3 molecules have M·W M_3

..... and so on

Then,

Number Average M·W ($\bar{M}_n$) of sample would be,

$$\bar{M}_n = \frac{n_1 M_1 + n_2 M_2 + n_3 M_3 + \ldots}{n_1 + n_2 + n_3}$$

$$= \frac{\sum n_1 M_1}{\sum n_1}$$

Similarly DP can also be calculated,

$$\bar{DP}_n = \sum \frac{n_1 (D P_1)}{n_1}$$

Also,

$$\bar{M}_n = m \cdot (\bar{DP})_n$$

Where , m = Molecular weight of monomer in the sample.

4.3.3 Weight Average M·W ($\bar{M}w$)

For a sample

Let W = Weight with M_w as M·W.
W_1 = Weight with M_{w1} as M·W.
W_2 = Weight with M_{w2} as M·W. and so on,

$$\text{Then, } \bar{M}_W = \frac{\sum W_1 M_1}{\sum W_1} = \frac{W_1 M_1 + W_2 M_2 + W_3 M_3 + \ldots}{W_1 + W_2 + W_3 + \ldots}$$

$$= \frac{\sum n_1 M_1^2}{\sum n_1 M_1} \qquad \ldots(\text{as } W_1 = n_1 M_1)$$

Note : Generally $\bar{M}_W > \bar{M}_n$

- In the similar way other viscosity average molecular weight concept also can be derived.
- Determination of average molecular weights can be carried out as,

  (1) $\bar{M}_n$ by measurement of colligative properties such as elevation in b·p.

  (2) $\bar{M}_W$ by light scattering experiments which are used for molecular size determination.
- Finally polymers are categorised in following four forms, on the basis of their end uses.

	Form of polymer	Significant properties for end uses	Examples
A	Plastic	Plasticity, mouldability	PVC, PE
B	Rubbers	Elasticity, vulcanisability	Isoprene Neoprene
C	Resins	Resinous / Viscous fluid form, Ability to form cross-linked polymer.	PF, UF.
D	Fibres	Tensile strength	ropes strings nets.

4.3.4 Polymer Crystallinity

It is a property a polymer exhibits in varying extent, which is based on the pattern of arrangement of molecules of polymer.

A polymer is said to be 'crystalline' if all molecules are arranged in orderly compact manner with symmetrical orientation, with higher force of attraction between two chains.

Crystalline polymers generally,

1. Posses high density
2. Strong, hard but brittle
3. Have sharp M.P.

This property can be calculated by density measurement of sample and of other known highly crystalline to highly amorphous polymer. Then,

$$\%\text{ crystallinity} = \frac{\text{density of sample (d)} - \text{Density of highly crystalline (dc) polymer}}{\text{dc} - \text{da}}$$

4.3.5 Amorphous Polymer

Amorphous Polymer are generally hard and brittle; having random arrangement of molecules.

Properties of amorphous polymers

- **Structure :** Amorphous polymers have a random and coiled molecular structure.
- **Melting point :** Amorphous polymers don't have a sharp melting point and instead gradually soften when heated.
- **Dimensional stability :** Amorphous polymers are dimensionally stable.
- **Flow :** Amorphous polymers melt more evenly and have isotropic flow, which results in less shrinkage.
- **Strength :** The physical entanglement of the chains and the dipole secondary bonds between chains make amorphous polymers strong.
- **Resistance :** Amorphous polymers have good chemical resistance and are resistant to hot water and steam

Examples of amorphous polymers include:

1. Polymethyl methacrylate (PMMA)
2. Polystyrene (PS)
3. Polycarbonate (PC)
4. Polysulfone (PSU)
5. Polyvinyl chloride (PVC)

4.3.6 Solved Numericals

Ex. 4.3.1 : Calculate the number average molecular weight, if two polymers, having mass equal to 100 to 10000 are mixed.

Soln. :

$$\bar{M}_n = \frac{100 + 10000}{2} = 5050$$

Ex. 4.3.2 : Calculate the number and weight average molecular weights of a polymer sample containing 20% of polymer A and 80% of polymer B. The molecular weights of A and B are 3000 and 30000 respectively.

Soln. :

$$\bar{M}_n = \frac{0.2 \times 3000 + 0.8 \times 30000}{0.2 + 0.8} = 24600$$

For finding out $\bar{M}_n$ we have to calculate the number of molecules of A and B.

$$\frac{\begin{array}{c}\text{Number of molecules of B}\\ \text{having molecular mass 30000}\end{array}}{\begin{array}{c}\text{Number of molecules of A}\\ \text{having molecular mass 3000}\end{array}} = \frac{80 \times 3000}{20 \times 30000} = \frac{2}{5}$$

Thus for every 5 macromolecules of mass 3000, there are 2 molecules of mass 30000. Hence,

$$\bar{M}_n = \frac{5 \times 3000 + 2 \times 30000}{(5 + 2)} = 10714$$

Ex. 4.3.3 : If 1000 g of a polymer of molecular weight 1000 g/mole is mixed with 1000 g of another polymer of molecular weight 10^6 g/mole, what is the ratio of $\bar{M}_w/\bar{M}_n$.

Soln. :

Polymer	Weight	Mol. wt.	No. of moles in
1	1000 g	1000 g/mol	$1(n_1)$
2	1000 g	10^6 g/mol	$10^{-3}(n_2)$

$$\bar{M}_n = \frac{n_1M_1 + n_2M_2}{n_1 + n_2} = \frac{(1 \times 1000) + (10^{-3} \times 10^6)}{1 + 10^{-3}}$$

$$= \frac{2000}{1.001} \approx 2000$$

$$\bar{M}_w = \frac{n_1M_1^2 + n_2M_2^2}{n_1M_1 + n_2M_2} = \frac{1 \times (1000)^2 + 10^{-3} \times (10^6)^2}{(1000 + (10^6 \times 10^{-3}))}$$

$$= \frac{10^6 + 10^9}{1000 + 1000} = \frac{10^6(1 + 10)}{2000} = 5.5 \times 10^5$$

$$\frac{\bar{M}_w}{\bar{M}_n} = \frac{5.5 \times 10^5}{2000} = 2.75 \times 10^2$$

Ex. 4.3.4 : A polymer has the following molar mass.

Number of molecules	Molar mass (g/mol)
50	5000
75	6000

Calculate the number average, weight average and PDI.

Soln. :

$N_1 = 50, \; M_1 = 5000$

$n_2 = 75, \; M_2 = 6000$

$$\bar{M}_n = \frac{\sum n_iM_i}{\sum n_i}$$

$$\bar{M}_n = \frac{n_1M_1 + n_2M_2}{n_1 + n_2}$$

$$\bar{M}_n = \frac{(50 \times 5000) + (75 \times 6000)}{50 + 75}$$

$$= \frac{250000 + 450000}{125}$$

$$= \frac{700000}{125} = 5600 \text{ g/mol}^{-1}$$

$$\bar{M}_w = \frac{\sum n_iM_i^2}{\sum n_i M_i}$$

$$= \frac{50(5000)^2 + 75(6000)^2}{(50 \times 5000) + (75 \times 6000)}$$

$$= \frac{125 \times 10^7 + 270 \times 10^7}{7 \times 10^5}$$

$$= \frac{395 \times 10^7}{7 \times 10^5} = 5642 \text{ g/mol}^{-1}$$

$$\text{PDI} = \frac{\bar{M}_w}{\bar{M}_n} = \frac{5642}{5600} = 1.0075$$

Ex. 4.3.5 : An equal number of protein mixture containing Haemoglobin kg/mol, Ribonuclease 13.7 kg/mol, Myoglobin 17.2 K. Calculate the number average and mass average mole weight of the protein solution.

Soln. :

$$\left.\begin{array}{l} \text{Heamoglobin} = 15.5 \text{ kg mol}^{-1} \\ \text{Ribonuclease} = 13.7 \text{ kg mol}^{-1} \\ \text{Myoglobin} = 17.2 \text{ kg mol}^{-1} \end{array}\right\}$$

Molecules are in Equal number

$n_1 = n_2 = n_3 = n$

$\frac{1}{3} = 0.333$

$$\bar{M}_n = \frac{\sum n_i M_i}{\sum n_i}$$

$$= \frac{(n \times 15.5) + (n \times 13.7) + (n \times 17.2)}{n + n + n}$$

$$= \frac{\cancel{n}\,(46.4)}{3\cancel{n}}$$

$$\bar{M}_w = \frac{\sum n_i M_i^2}{\sum n_i M_i}$$

$$= \frac{n(15.5)^2 + n(13.7)^2 + n(17.2)^2}{(n \times 15.5) + (n \times 13.7) + (n \times 17.2)}$$

$$\frac{n\,[240.25 + 187.69 + 295.84]}{n\,[15.5 + 13.7 + 17.2]}$$

$$= \frac{\cancel{n}\,[240.25 + 187.69 + 295.84]}{\cancel{n}\,(46.4)}$$

$$= 15.59 \text{ Kg/mol}^{-1}$$

4.4 Plastics

- These ***high polymers*** are the substances with high molecular weights which may occur in nature or be synthesized.
- The name plastic refers to its meaning that these are the polymers which mould themselves into articles by heat and pressure.
- As mostly plastics are synthetic these are also know as *synthetic resins.*
- Over the years the plastics have taken the place of metal in various uses.

4.4.1 Classification of Plastics

On the basis of setting manner in final stage of manufacture the plastic materials or plastic articles are classified in two classes ;

(i) Thermo plastic
(ii) Thermo setting

The characteristics of these two types is given below.

4.4.1(A) Thermo Plastics or Thermosoftening Plastics

- These show reversible change on heating i.e. they soften on heating but regain their original properties on cooling.
- They gain or lose hardness with rise or fall in temperature. Their chemical nature does not get affected even on repeated heating and cooling, i.e. the changes are more of physical nature.
- If these resins are softened, they retain their softness at that temperature.
- These resins can be reclaimed from waste, and they are soft, weak and less brittle.
- The method usually used to manufacture polymers is addition polymerisation.
- They are generally long chain linear polymers with occasional or no cross linking.
- They are soluble in specific organic solvents.
- Examples of this class of resins are cellulose nitrate, polyacrylates, ethyl cellulose, polyvinyl resins, styrene or polystyrene resins, polyamides (nylons) polyethers, polypropylene, polyethylene etc.

4.4.1(B) Thermo Setting Plastics

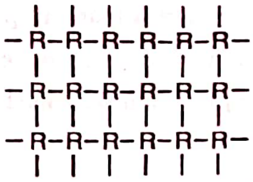
Q. Thermosetting polymers cannot be reshaped and reused. Give reasons. **May 16, 3 Marks**

- These are the polymers, which on heating change irreversibly into hard and rigid materials.
- The melt of this polymer when set into a mould to form an article, is almost a permanent set.
- On reheating the article does not soften again, thus inhibiting irreversibility.
- They are hence known as *thermo hardening plastics* or *permanent setting resins* and during moulding acquire three dimensional cross linked structure with strong covalent bonds.
- On reheating, these bonds retain their strength and hence such a plastic does not soften on reheating.
- Thermo setting plastics cannot be reclaimed from waste due to their irreversibility.
- They are hard, strong and brittle than thermo plastics.
- The method by which these are formed is called as *condensation polymerisation*.
- They are insoluble in almost all organic solvents, due to their cross linked three dimensional structure.
- Phenol formaldehyde / bakelite, amino plastics, alkyl plastics, epoxy plastics, silicon plastics etc. are the best known examples of *thermosets*.

4.4.2 Comparison of Plastics

Q. Distinguish between thermoplastic and thermosetting polymers.

Dec. 15, Dec. 16, May 17, Dec. 17, Dec. 18, 3 Marks

Sr. No.	Thermoplastics or Thermosoftening Plastics	Thermosetting Plastics or Thermohardening Plastics
1.	These are formed by *addition Polymerisation.*	These are formed by *condensation Polymerisation* only.
2.	They are long chain linear polymer with negligible cross links.	These have three-dimensional network structure with number of cross links.
3.	Structural formula −R−R−R−R−R−R−R−R−	*Structural formula :* 

Sr. No.	Thermoplastics or Thermosoftening Plastics	Thermosetting Plastics or Thermohardening Plastics
4.	Monomer used in these is generally bifunctional.	In this, monomer used is Tri, Tetra or polyfunctional.
5.	They have low molecular weight.	They have high molecular weight.
6.	They are usually soft, weak and less brittle.	They are usually hard, strong and more brittle.
7.	They are usually soluble in some organic solvents.	Due to strong bonds and cross links, they are insoluble in almost all organic solvents.
8.	They get softened on reheating readily because secondary forces between the individual chain can break easily by heat or pressure.	They do not soften on reheating because the cross links and bonds retain their strength on heating.
9.	They can be softened, reshaped and thus reused. (reclaimed from waste) (by reheating to a suitable temperature).	They retain their shape and structure even on heating. Hence, they cannot be reshaped and reused. (cannot be reclaimed).
10.	Example : Polyethylene, polystyrene, PVC, PVA	Example : Phenolformadehyde, ureaformaldehyde, Nylon 6 : 6.

4.5 Glass Transition Temperature (T_g)

Q. Explain glass transition temperature of polymer. **May 15, May 16, Dec. 18, May 19, 3 Marks**

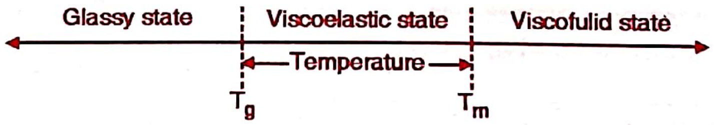
Q. Write short notes on Glass transition temperature. **Dec. 17, May 18, 3 Marks**

- When a **plastic or rubber is cooled** upto certain temperature, it becomes so hard and brittle that it breaks into pieces like glass, on application of stress.
- **Definition :** The temperature below which the polymer becomes hard, brittle and glassy and above which it is softer and flexible, is known as glass transition temperature.

4.5.1 Effect of Temperature on Polymer

Q. Discuss the effect of temperature on polymers. **May 19, 3 Marks**

- The hard and brittle state is the glassy state and soft-flexible state is the viscoelastic state. If the viscoelastic state of polymer is heated further, the polymer becomes a viscous liquid and can flow. This state is known as viscofluid state.



- Below T_g the molecules in polymer do not move apart and do not have movements within the molecular chains.
- Therefore stress transfer property is lost and polymer below T_g is brittle.
- Above the T_g, the chain segments within the long molecules move locally like a person moving his hands, legs, leaning forward- backward but standing at one place, during exercise. Thus the polymers in the viscoelastic state have flexibility or stress transfer property.
- Above the temperature T_m; the kinetic energy of the polymer molecules is high enough to cause movement within the chain segments as well to move from one position to another. Therefore this state has flow character like liquids.

- Some polymers have thermal degradation at and above T_m.

Polymer	T_g °C	T_M °C
Polyethylene	– 125	115
Polypropylene	– 18	175
Polystyrene	100°C	240°C
Polyvinyl chloride	80	212
Polyacrylonitrile	97	241

4.5.2 Factors Affecting T_g

Q. What are the factors that affect Glass transition temperature? **May 16, 3 Marks**

(1) **Crystallinity :** Higher the crystallinity of polymer, **higher** is its T_g value. Amorphous polymers have lower T_g.

(2) **Molecular weight :** Higher the molecular weight of a polymer, **greater** is the T_g of the polymer. However, T_g value depends upon molecular weight upto 20,000, for vinyllic polymers and after that there negligible effect.

(3) **Side groups on chain :** Presence of bulky side groups on the polymer chain, increases the T_g value. E.g. polyethylene has no side groups on chain and has T_g of – 125°C while polystyrene has $-C_6H_5$ groups on the chain and has much higher T_g of 100°C. Bigger sized side groups and greater polarity of the side groups have larger effect on T_g value.

(4) **Cross linking of polymer chains :** The T_g of a polymer **increases** with higher extent of crosslinking of polymer chains.

(5) **Plasticizer effect :** Addition a plasticizer of polymer **decreases** the T_g of polymer. Because, the polymer becomes amorphous and there is increase in chains mobility.

(6) **Coiled polymer chains :** The polymer having coiled or spring like chain structure, shows **lower** T_g. e. g. rubbers.

(7) **Force of attraction between chains :** The polymers having stronger force of intermolecular attraction, have **greater** T_g, as the chains mobility is lesser in such cases.

A polymer having higher T_m, is difficult for melt processing.

T_g and T_m are approximately related as $3\,T_g \approx 2\,T_m$.

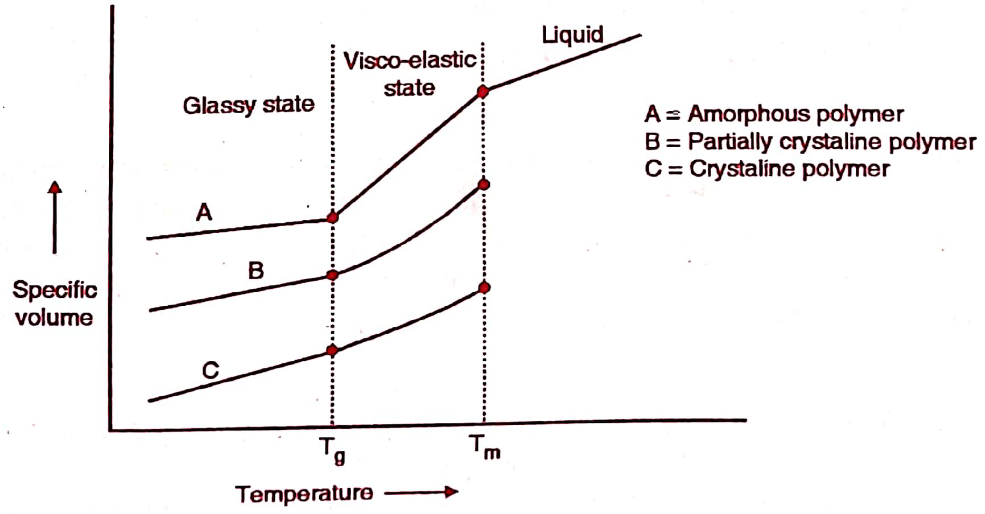


Fig. 4.5.1 : Effect of cooling on specific volume of polymer

4.5.3 Importance Significance of T_g

Q. What is the significance of Glass transition temperature? **May 15, May 16, Dec. 18, 2 Marks**

A polymer below its T_g, is hard, stiff and brittle and therefore it is not preferred material for use at temperature below its T_g. In general, **a polymer material should have much lower T_g than the operating temperature.** e.g. polymers to be used for refrigerators, air conditioners or used in cold countries, should have lower T_g, so that they will not break during use.

4.6 Mechanical Properties of Polymers

Polymers possess : physical properties like :

(i) Solubility

(ii) Effect of heat

(iii) Diffusion and permeability

Mechanical properties like :

(i) Toughness

(ii) Strength/tensile strength

(iii) Elasticity

1. Hardness

It is a measure of "Resistance" of a polymer to scratching and the deformation under applied force. It is important for selecting the polymer for its use as packaging, automotive components or in medical. The hardness / toughness of a material is typically determined using the area under the stress and strain curve. It measures the energy absorbed by the material before it breaks.

2. Strength of polymer

- It is determined by measuring "the stress required to cause a break". There are numerous types of strength, namely tensile (stretching of the polymer), compressional (compressing the polymer), flexural (bending of the polymer), torsional (twisting of the polymer), impact (hammering).
- **Strain** is measured by the percentage change in the length of the material before fracture. It is also a measure of ductility. Young's Modulus (Modulus of Elasticity or Tensile Modulus) is "the ratio of stress to the strain in the linearly elastic region. Elastic modulus is a measure of the stiffness of the material".

$$E = \text{Tensile Stress/ Tensile Strain.}$$

3. Tensile strength

It is a measure of the strength of polymer to withstand stress before breaking when stretched/pulled. It is important for fibers. In the case of polymers, tensile strength is an essential property, especially for applications where the material is expected to endure stretching forces. For example, fibers used in textiles or ropes must exhibit high tensile strength to perform effectively under load. The tensile strength is typically expressed in Pascals (Pa) or pounds per square inch (psi).

4. Creep

It is property that describes the tendency of polymer to get deformed permanently under constant stress. When a load is put on a body made from a polymer it will be deformed. This deformation is time dependant, as shown in the figure below and consists of two parts: (i) An elastic deformation that occurs immediately after applying the load. (ii) A plastic deformation that grows in time for the duration of the load.

5. **Fatigue**

It is the damage suffered by polymer on its surface due to friction under repeated stresses applied. Stress can be due to thermal or mechanical. Polymer softens under thermal fatigue and suffers cracks under mechanical fatigue.

6. **Impact Resistance**

It is property which is a measure of a materials ability to tolerate with stand sudden forces without cracking/breaking. Impact resistance is measured using different testing methods like charpy and IZOD impact tests.

4.7 Electrical Properties

Electrical properties of polymers are related to dielectric and electrical conductivity. Polymer is expected to be a good insulator, rather than good conductor.

(i) Dielectric Strength

This property describes the strength of a polymer to sustain electrical field i.e. to act as an insulator. The unit to measure DS-is volts per unit thickness.

Higher DS-Better Insulation property

DS is direct current voltage between two electrodes at the point of dielectric breakdown. This indicates how good is the polymer material to be used as "Insulator".

(ii) Insulation Resistance

- This serves as a "designation" for electrical resistance of cables, electrical systems and of lines. It is measured in ohms.
- This is extremely important because it is related to protection of persons against electric shocks and excision of materials and property damage due to leaking currents if any.
- For this purpose, (i) Thermoplasts compounds like PE, PVC, (ii) Thermoplasts sheathing compounds like PVC, MDPE, HDPE, Nylon are used. SI unit of Insulation Resistance is mega ohm.

(iii) Surface Resistivity (SR)

- Surface Resistivity (SR) is a measure of "resistance of surface," of the polymer to "flow of electric current."
- It also is a measure of resistance to leakage of current along the surface of an Insulating material.
- Higher SR – lower leakage and material is less conductive

e.g. SR of PE = 1016 ohms

PP = 10

Intrinsic undoped Silicon = 1000 to 10000 ohm-cm.

Doped silicon wafers = 0.001 ohm-cm.

4.8 Optical Properties

The properties like gloss, transparency, clarity haze, colour, surface aspect and refractive index fall under optical properties of polymers.

Optical Properties : Fundamentals

Dielectric Constant

A dielectric material can store electrical charge and can develop an electric field. The polymers are used as insulating materials, and are used to insulate wires. The polymers are are used as dielectric materials.

Refractive index

The refractive index of a polymer is "a measure of how the speed of light changes as it travels from a vacuum into a material". Thus the refractive index defines "how much light is bent or "refracted" when crossing into different mediums". Overall, the refractive index, n, is defined as: n = c/v where, c = velocity of light in a vacuum; v = velocity of light in the new medium

a) When light enters new medium from a vacuum, it decelerates due to the interaction of the electric and magnetic fields of light with the properties of the new material.

b) As the speed of light is fastest in a vacuum, the refractive index of a vacuum is 1 and is thus used as the reference standard against all other mediums. According to Maxwell's equations, the refractive index, n, of a non-magnetic material is dependent on the dielectric constant of the material : $n = (\varepsilon)\ 1/2$ (2.3) where, ε = dielectric constant of the material. The refractive index is also dependent on the optical frequency or wavelength which is called chromatic dispersion. In general, the refractive index increases

- With shorter wavelengths
- With higher Temperature
- With mechanical stresses
- With presence of impurities,(Doping) scattering phenomena play a major role in determining optical properties

Colour and IR absorption

Most polymers are colorless but a few pure polymers absorb radiation in the visible spectrum, roughly between 380 and 760 nm, resulting in colour development.

Transmittance

- Transmittance is defined as "the ratio of the transmitted radiant flux to the incident radiant flux in a medium".
- It is a dimensionless number that, like reflectance, ranges from 0 to 1 for nonfluorescent materials, with the total transmittance being the sum of regular and diffuse transmittance.
- Transmittance is the quantity of light that passes through a solution. the ability of a solution or a layer of a substance to absorb radiation that is expressed mathematically as the negative common logarithm of the transmittance of the substance or solution. called also optical density. to regulate the light transmission, save against the heat, and provide clear visibility.
- Transmittance (T) is the fraction of incident light which is transmitted. In other words, it's the amount of light that "successfully" passes through the substance and comes out the other side. It is defined as $T = I/Io$, where I = transmitted light ("output") and Io = incident light ("input").

Photoelectric effect

- Photoelectric effect, is "the phenomenon in which electrically charged particles are released from or within a material when it absorbs electromagnetic radiation". The photoelectric effect in polymers has been studied in the context of composite heterostructures, which are made up of both polar and non-polar polymers. The photoelectret effect is a phenomenon that occurs in composite heterostructures made of polar and non-polar polymers. The polarity of the polymer matrix affects the difference in photoelectret potentials in a given volume share of the inorganic phase.
- The effect is often defined as "the ejection of electrons from a metal plate when light falls on it".
- The photoelectric effect is dependent upon various factors such as;

1. Frequency of light,
2. Intensity of light,
3. Nature of material,

4. Energy of light
5. Potential difference.

- **Principle :** The photoelectric effect is the emission of electrons or other free carriers when light shines on a material. Electrons emitted in this way can be called photo electrons.
- There are two types of PE effect:
  1. the internal photoelectric effect and
  2. the external photoelectric effect.
- PE effect can explain following which cannot be explained by Wave theory
  - i. Maximum kinetic energy of emitted electrons is independent of the intensity of incident light.
  - ii There exists a threshold frequency for each photosensitive material.
  - iii Photoelectric effect is instantaneous in nature.

Applications of the photoelectric effect

1. In "electric eye" door openers,
2. light meters used in
   - a) Photography
   - b) Solar panels
   - c) Photostatic copying.
   - d) Polymer-based functional materials
   - e) Imaging technology
   - f) Photoelectric sensors.

Important Terms and Definitions

- The compounds formed by large number of small molecules (called monomers) linked together are known as *polymers* [poly = many].
- Polymers which are isolated from natural materials are called as natural polymers. E.g. silk, Wool, natural rubber, cellulose, starch, proteins etc.
- The polymers obtained by simple chemical treatment of natural polymers to improve their physical properties like lustrous nature, tensile strength are called semisynthetic polymers.
- Polymers synthesized in laboratory from low molecular weight compounds, are called as, synthetic polymers.
- **Homopolymers :** The macromolecules formed by identical monomers, are known as *homopolymers* and those with different monomers are known as *mixed polymers or co-polymers.*
- **Hetero / mixed / Co-polymers :** These are the compounds formed by two *different small molecules.*

  For example in polystyrene butadiene, one molecule of butadiene combines with one molecule of styrene. The product obtained acts as a monomer to get the polymer.
- **Sub classification :** On the basis of arrangement of monomeric units in polymer, these are named as *linear, branched or cross linked* (three dimensional structures).
- **Regular / Irregular copolymers :** Co-polymer is named as *regular or irregular* on the basis of arrangement.

  E.g. – A – B – A – B – A – B – A – B – A – Regular

  – A – B – B – A – B – A – A – B – B – Irregular
- **Block copolymer :** If co-polymer chain possesses relatively long sequence of like monomers, it is called as *block co-polymer*

- **Graft copolymer :** If co-polymer possesses branched structures in which the monomer segments are not in same sequence on branch and backbone, it is known as *graft co-polymers.*
- **Isotactic :** In *isotactic*, the head to tail configuration in macromolecule with respect to functional group is iso, i.e. all the functional groups lie on the *same side* of the chain.
- **Atactic :** In *atactic*, the head to tail configuration is *random* i.e. the functional groups are arranged randomly.
- **Syndiotactic :** In *syndiotactic polymers*, the functional groups occupy the alternating position.

  The physical properties of polymers vary, on the basis of the position in which a functional group is attached in macromolecule.
- **Definition:** The temperature below which the polymer becomes hard, brittle and glassy and above which it is softer and flexible, is known as glass transition temperature.

Review Questions

Q. 1 What are polymers? How are they classified?

Q. 2 Discuss chemical bonding in polymers.

Q. 3 Explain classification of polymer on the basis of source and structure.

Q. 4 Differentiate between thermoplastic and thermosetting polymers.

Q. 5 Differentiate between addition and condensation polymerization.

Q. 6 Explain classification of polymer on basis of monomer.

Q. 7 Discuss natural and synthetic polymers with suitable examples.

Q. 8 Write a short note on homo- and hetero polymers.

Q. 9 Discuss organic polymers with suitable examples.

Q. 10 Write short note on average molecular weight of polymers.

Q. 11 Explain classification of polymer on the basis of monomer.

Q. 12 Write a short note on glass transition temperature of polymer.

Q. 13 What are the factors influencing glass transition temperature of polymer.

Q. 14 Discuss weight average and number average of polymer.

Q. 15 Discuss properties of amorphous polymers with examples.

Q. 16 Define glass transition temperature. Write a short note on significance of glass transition temperature.

Q. 17 Discuss in detail effect of temperature on polymers.

Q. 18 Discuss mechanical properties of polymers.

Q. 19 Write short note on (i) Dielectric strength (ii) Insulation resistance (iii) Physical resistivity

Q. 20 Explain photoelectric effect in polymer.

□□□

5

Introduction to Composites

Syllabus

A) Definition, Characteristics of Composites,

B) Constituents of Composites - Matrix Phase and Dispersed Phase (Definition and Functions)

C) Classification of Composites.

5.1 Introduction

- *Composites are engineered materials,* comprising of *metals, ceramics, glasses and polymers.* The relationship between these three constituents with respective examples is shown in Fig. 5.1.1.

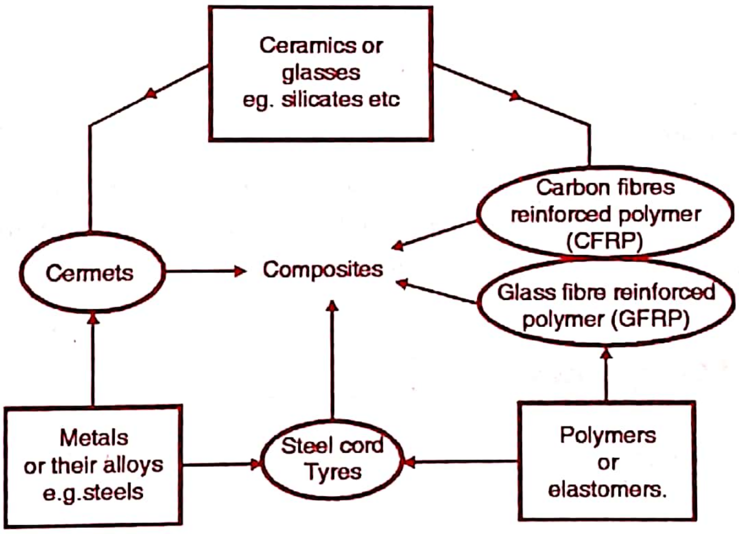

Ceramics or glasses eg. silicates etc
Carbon fibres reinforced polymer (CFRP)
Cermets
Composites
Glass fibre reinforced polymer (GFRP)
Metals or their alloys e.g.steels
Steel cord Tyres
Polymers or elastomers.

Fig. 5.1.1 : Engineering materials forming composites

- The composites obtained using respective material exhibits *unique properties or qualities.*
- The composites show better characteristics as compared to those possessed by its constituents.
- Sometimes all together new/different characteristic is observed to be possessed by composite material which is not present in either of its constituents.
- The combination of two or more existing materials is brought about by physical means. A composite in true sense must show *matrix material surrounding its reinforcing material* completely, in which the *two phases,* not only exist, but *act together* so as to produce the *desired characteristics.*

Examples

- Natural composite such as,
  - Wood or many other plant tissues contain cellulose chain polymer in a matrix of lignin.
  - *Bone* which contain soft but strong protein collagen and hard and brittle material apatite.

- Synthetic composites such as,
  - Rain proof cloth (cloth impregnated with waterproof material),
  - Packing paper impregnated with bitumen or wax,
  - Reinforced concrete,
  - Insulating tape are some examples.

5.1.1 Definition of Composites

- Thus composite may be defined as, "A multiphase product made by using two or more existing materials which exhibits properties of its constituents as well as shows certain unique properties of its own."
- The properties of composite solely depend upon the composition of its constituents. Thus it is possible to form newer composites as per demand of technologies, such as in the field of :
  - (i) Aerospace
  - (ii) Marine
  - (iii) Transportation

  } Applicatn

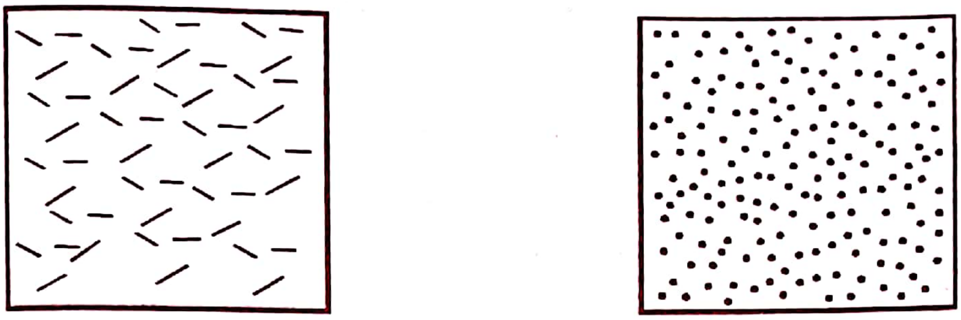
- For aerospace applications, the material with certain specific properties is required. Such a material should have following properties,
  - (i) Low density
  - (ii) High stiffness
  - (iii) High strength
  - (iv) High resistance to abrasion.

  } Charachristic

- All above properties are *contradictory* to each other like *to have high strength, density has to be high*. But *if* we combine a material of *low density* with other one with high strength and other properties, we can make a new material having all above properties. Such a new material is prepared by composing, hence called as *"composites"*.

5.2 Constitution of Composites

- Most of composites are made by using minimum two phases. The phases are namely :
  - (a) Matrix phase
  - (b) Dispersed phase.
  - e.g. polymer composites in which matrix is of polymer and particles of metals/ceramic/fibre serves as dispersed phase.
- A *polymer* and a *reinforcing material* as a two phase mixture, with interfaces between them, is known as polymer composite.
- The polymer composite has properties of both the materials in combination.
- The polymer phase is called as *matrix* phase and the composite used for mixing is known as *dispersed phase*. The boundaries between the matrix and dispersed phase, are known as *inter phase*.
- On the basis of the dispersed phase used in the matrix, the polymer composites are of two types :
  - (A) Fibre reinforced
  - (B) Particle reinforced.



(A) Fibre reinforcement (fibres in polymer matrix) **(B) Particle reinforcement (particles in polymer matrix)**

Fig. 5.2.1

5.2.1 Matrix Phase

- *Matrix material* should have the properties such as :
  1. It should have adequate ductility.
  2. Its should possess lower elastic modulus as compared to that of the fibre used.
  3. It should *get bonded to fibre* very strongly, but with minimum pull out of fibre.
- The matrix material is selected on the basis of the properties mentioned in combination of the fibre. The proper choice of matrix and fibre gives *strong bonding* and ultimately a *good composite material.* ①

Examples

Metals such as Al, Cu which show high ductility bonded to the polymers such as thermoplastics and thermosets are most widely used as matrix material.

Functions of Matrix

Functions of matrix constituent in polymer composite are,

(i) *To bind* the reinforcing particles/fibres *strongly.*

(ii) It acts as medium for distribution of applied load to the dispersed phase.

(iii) It keeps the reinforcing *fibres in proper orientation* for the high strength development.

(iv) It *prevents* propagation of *cracks* due to its plasticity.

5.2.2 Dispersed Phase

- *The dispersed phase* comprises of fibres, normally with small diameter preferred to bulk ones. A special type of fibres, widely known as *Whiskers* are used.
- These fibres have following properties : [Properties of whiskers]
  1. They are very thin single crystal.
  2. They possess extremely large length/diameter ratios.
  3. They are flaw free.
  4. They are small in size, hence the degree of crystalline perfection obtained is high.
  5. They are exceptionally strong.
- All above properties make *whiskers highly useful* as reinforcing fibres as dispersed phase. But still these are not used very commonly, due to following reasons,
  1. They are costly.
  2. The process of incorporating them in matrix phase is tedious.

- Examples of whiskers are *oxides* (of Al), *carbides* and *nitrides* (of Si), *Graphite etc.*
- The other simple fibre materials used as *dispersed phase* are :
  1. Polycrystalline polymers or ceramics.
  2. Amorphous polymers or ceramics.
- Both above generally have *small diameters*, hence *preferred.*
- Some important dispersed phase examples and their characteristics are given below :

(a) Glass fibres

- The glass fibres are produced by passing a glass melt through small orifices (holes) and cooled.
- Glass fibres are popular reinforcing materials. It offers very high tensile strength, higher thermal stability, high toughness and impact strength, to the polymer matrix.
- Polymers are filled with 20% to 40% glass fibres.

(b) Carbon fibres

- They are prepared from carbon by oxidation under tension at low temperature and then carbonization at 1000°C.
- These fibres are stiff, strong, even at high temperature.

(c) Aramid fibres

- Aramid is the aromatic polyamide e.g. Nomex, Kevlar.
- It has liquid-crystal polymer property.
- Its parallel arranged polymer chains for a long distance can be obtained from melt during drawing.
- The fibres have very high tensile strength; impact resistance, high thermal stability.

(d) Particles

- Metal powders, metal oxides, carbon black, metal carbides, silica powder, mica, salts, can be intimately mixed with the polymer matrix to make the composite.
- These materials offer high abrasion resistance, higher mechanical strength, better performance at higher temperature to the composite and may modify thermal and electrical conductivity of polymer.
- It is necessary that *the dispersed phase* should have *good compatibility* with the *polymer matrix* and there should be *strong interfacial bond* between the dispersed phase *and matrix phase,* otherwise the *composite* may *have low durability* and *easier failure* during working.

(e) Metallic wires such as *Molybdenum, Tungsten* or *High carbon* steel are also used as *dispersed phase.* These are more suitable for automobile tyres, wire wound high pressure hoses or filament wound rocket casting. Their specific uses are due to large diameter in wire form.

5.3 Characteristic Properties of Composite Materials

Composites are made from combination of metals, polymers and ceramics or only metals, and ceramics. They possess following unique characteristics over individually metal / polymers / ceramics.

(1) They possess

(i) Low specific gravity

(ii) High specific strength

(iii) High specific stiffness

(iv) Low Thermal expansion

(v) High corrosion resistance

(vi) High oxidation resistance

(2) They can retain their strength at high temperature.

(3) They show better toughness, impact and thermal shock resistance.

(4) They show better fatigue strength, and low thermal expansion and electrical conductivity.

5.4 Classification of Composites

The composites are classified on the basis of reinforcing material or structure as follows :

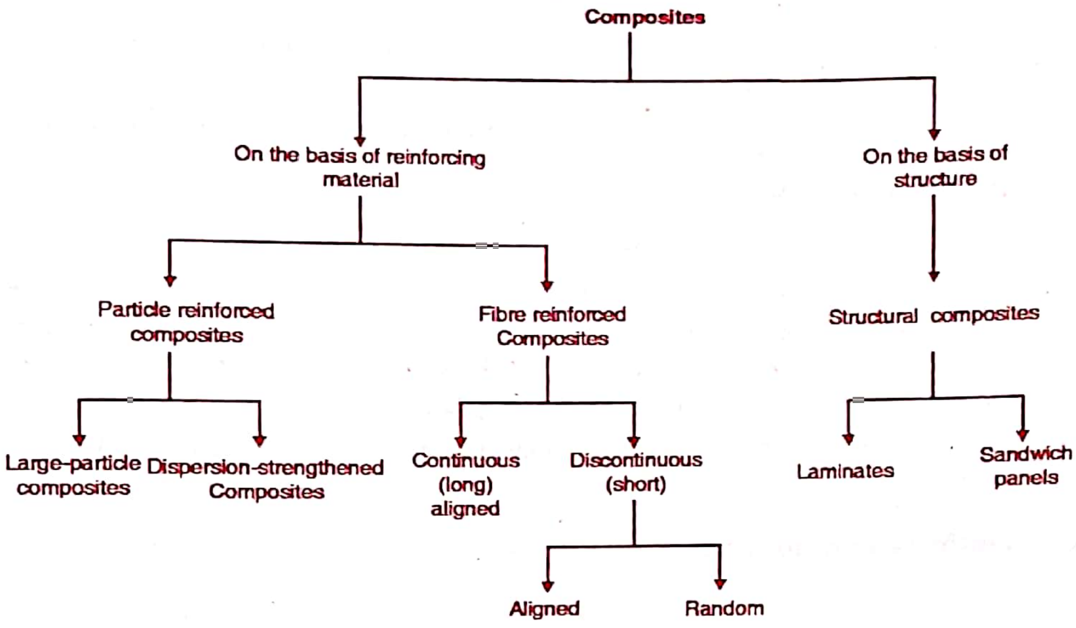

Composites
On the basis of reinforcing material
On the basis of structure
Particle reinforced composites
Fibre reinforced Composites
Structural composites
Large-particle composites
Dispersion-strengthened Composites
Continuous (long) aligned
Discontinuous (short)
Laminates
Sandwich panels
Aligned
Random

Fig. 5.4.1 : Classification of Composites

5.4.1 Particle-reinforced Composites

In this type of composites, the size of particles in dispersed phase are of nearly the same in all direction.

Large particle composites

In this sub-type of composites, the particulate phase should have following characteristics.

(a) *Stiffer* and *harder* as compared to matrix phase.

(b) It acts as reinforcing material.

(c) It *restrains the movement* of matrix surrounding to itself.

(d) The bond strength between two phases governs *mechanical properties* of *composite*.

Table 5.4.1 : Examples of particle reinforced composites

Material	Matrix phase	Particulate phase	Properties
1. Concrete	Cement	Sand and gravels	1. R.C.C. is harder than ordinary cement. 2. Sets well on surface thereby holding structures.
2. Cermets (a) Oxide based	Cr	Al_2O_3	1. Good strength. 2. Very good thermal shock resistance.

Material	Matrix phase	Particulate phase	Properties
(b) Carbide based	Co or Ni	Tungsten Carbide (WC) Or Titanium carbide (TiC)	1. Very hard 2. Very high surface hardness ***Application*** : In wire drawing dyes, valves and machine parts.
	Co or Ni	Or Chromium carbide (CrC)	High abrasion and corrosion resistance ***Application :*** In valves, spray nozzle pump parts etc.

Dispersion-strengthened composites

- In this type of composite, the particles size is smaller (10 to 100 nm).
- The metal or alloys are made into extremely small particle size in given range and are dispersed in the matrix phase. This is achieved by appropriate heat treatment. The process is called as *"precipitation hardening"* or *"Age hardening"*, the former term given because the new phase of materials obtained in process is known as *"precipitates"*, where as latter term is suitable because composite increases its hardness as alloy ages.

  e.g. Alloys such as, *Cu – Sn, Mg – Al, Cu – Be, Al–Cu,* some ferrous *alloys* are hardened and made into composite materials with *ceramics.*

5.4.2 Fibre Reinforced Composites

Constitution

- These are composite materials made up of
  - (a) A polymer matrix
  - (b) A filament
  - (c) A bonding agent (which ties fibre filaments to polymers)
- Commonly used fibres are *glass or metallic.* These fibres are employed either in continuously or discontinuously as staples or whiskers.

Properties of fibre reinforced composites

- The fibre reinforced composites possess,
  - (1) High tensile strength
  - (2) High specific gravity
  - (3) High elastic modulus
  - (4) They are stiff.
  - (5) They possess lower overall density.
- Factors governing properties of fibre-reinforced composites are :
  - (1) Nature of fibres and matrix.
  - (2) Properties of fibres and matrix.
  - (3) Relative volume fraction of fibre and matrix.
  - (4) Orientation and distribution of fibres in matrix phase.

(5) Length to diameter ratio of fibres

(6) Strength of interfacial bond between fibre phase and matrix.

- Few important types of fibre reinforced composites, are given in Table 5.4.2, with properties and application.

Table 5.4.2 : Important fiber reinforced composites

Composite	Fibre phase	Matrix phase	Properties	Application	Limitation
1. Glass fibre reinforced polymer composite	Glass fibres (long as well as short)	Ploymers such as nylons, polyester etc.	1. Lower density 2. Higher tensile strength 3. Higher impact resistance 4. High resistance to corrosion and chemicals	1. Automobile parts 2. Pipes 3. Transportation industries 4. Industrial flooring 5. Storage tanks.	1. They can be used in low temperature service conditions; because polymers matrixes get deteriorated at higher temperatures. 2. The stiffness is comparatively low, hence cannot be employed as structural components.
2. Carbon fibre reinforced polymer composite	Glass fibres (long as well as small)	Polymers such as nylons, polyester etc.	1. Higher density 2. Excellent resistance to corrosion 3. Dimensional stability even at high temperature	1. Used to make structural components e.g. body or wings of aircraft helicopter. 2. Sports materials or fishing rods	High cost, hence used generally for specific purposes only.
3. Aramid fibre-reinforced polymer composite.	(a) Short aramid fibres or discontinuous	Polymeric material	1. High surface area. 2. High aspect ratio 3. Toughness to strength 4. Heat stability 5. High resistance to wear.	In automobile brakes and clutches.	Price is high, due to high cost of raw materials . **Note :** These are about 4 times more in performance than that containing asbestos. Hence are best substitutes in place of asbestos containing material which is banned due to its ill effect on health

Composite	Fibre phase	Matrix phase	Properties	Application	Limitation
	(b) Long aramid fibres continuous	Polymeric material	1. Ductile like metals 2. It can sustain stresses.	1. In commercial aircrafts 2. Helicopter parts like rotor blades, motor housing 3. Business aircrafts as structural material 4. Protective apparel (thermal or ballistics)	Practically on limitations except cost. **Note :** In latest commercial aircrafts (like Boeing–747 and Airbus 320), about 3-5% composites containing aramid or its hybrid fibres with carbon are employed.
4. Alumina and /or carbon fibre-reinforced metal composite	(a) Al_2O_3 or Carbon fibres	Aluminium Alloy	1. Low density 2. Resistant to thermal distortion 3. Resistant to wear 4. Creep resistant	To make engine components in automobile industry	
	(b) Al_2O_3or W (tungsten)	Ni and cobalt based alloy	1. Excellent strength 2. Resistant to creep and rupture at high temperature.	To make components of turbine engine	

5.4.3 Structural Composites or Layered Composites

A structural composite consists of both homogeneous and composite materials. Their properties depend upon, the characteristic properties of the constituent materials as well as the geometric design.

Structural composites are of two types such as,

(a) Laminar composite : e.g. *plywood*

(b) Sandwich panel : e.g. *honeycomb core*

5.4.3(A) Laminar Composites

- It consists of *panels or sheets* which are two dimensional. These panels possess *preferred directions to achieve high strength.*

  e.g. plywood in which wood and continuous aligned fibre reinforced plastics are in preferred directions.

- Such successively oriented layers are stacked one above other with preferred directions (Fig. 5.4.1) and then are cemented. Such an arrangement or orientation ensures varying high strength with each successive layer.
- Plywood is a laminated composite containing thin layers of wood where layers are alternatively glued together. This type of layering brings grain of each layer at right angles of its neighboring layer.
- Use of fabric material such as cotton, paper or woven glass fibres dispersed in suitable plastic matrix is also in practice to make laminar composites.

Properties

- Properties of these composites depend upon :
  (a) The properties of its constituents
  (b) The geometrical design
- Generally such composites are :
  (1) Strong in both directions of reinforcement
  (2) Low shear strength

Applications

These composites are used in many familiar applications, such as :

(1) Interiors in premises
(2) False ceilings for diffused lighting etc.
(3) Furniture making.

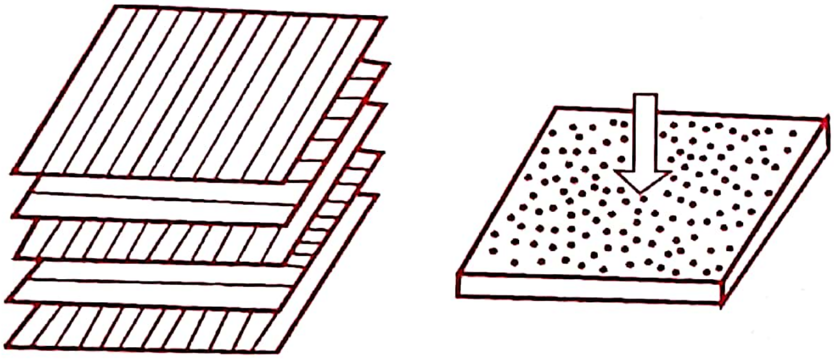

(a) (b)

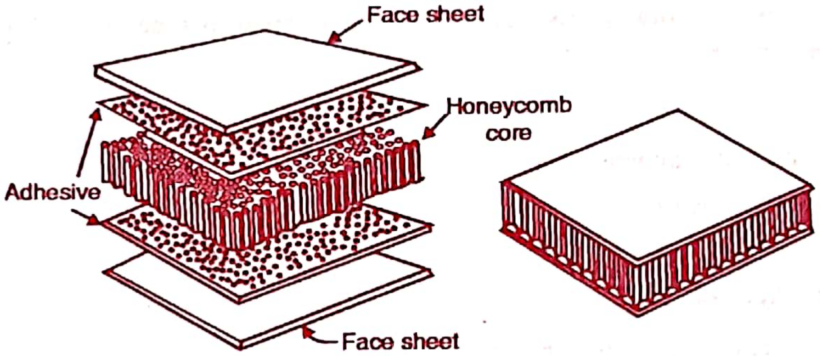
Fig. 5.4.1 : Oriented fibre-reinforced layers stacked successively for producing a laminar composite

5.4.3(B) Sandwich Panel

- This is another type of *layered composite.* It consists of
  (1) *"Faces"* are formed by two strong outer sheets.
  e.g. Titanium, steel, aluminium alloys, plywood, fibre reinforced plastic material.
  (2) *"Core"* which is layer of less dense material.
  e.g. Synthetic rubbers, foamed polymers, inorganic cementing material etc.
- All above three layers are joined together with an adhesive.
- In these *"faces"* are capable of bearing *transverse bending stresses.* The *'core'* performs functions related to structural properties.
  (i) Separation of faces from each other.
  (ii) Resisting deformations perpendicular to the face plane.

(iii) Providing certain degree of shear rigidity along above planes which are perpendicular to the 'faces'.

- With increase in thickness of core, its stiffness increases. The Fig. 5.4.2 shows 'honeycomb' structure which contain thin foils forming interlocked hexagonal cells with their axes oriented at right angles in the direction of face sheet.



(a) Honeycomb core sandwich panel : Construction

(b) Sandwich panel : Fabricated

Fig. 5.4.2 : Schematic diagram

Properties

These have following properties :

(1) Excellent dimensional stability

(2) Resistant to abrasion and corrosion

(3) High tensile strength

(4) Low density

(5) High elasticity modulus

Application

These are used in :

(1) *Aircraft* for wings, fuselage and skins of tailpane.

(2) *In roofs*, walls and floor of buildings.

5.5 Applications of Composite Materials

The composite materials find variety of applications in all those areas where, high mechanical strength, dimension stability, thermal stability, corrosion resistance, abrasion resistance etc. is desirable. They find application in following industries,

(a) Construction

(b) Electrical and electronics and telecommunication

(c) Transportation

(d) Agriculture

(e) Sport goods

(f) Automobile

(g) Aviation Industry

(h) Mobiles

Composites, in short are extremely useful and more research work is going on to develop newer materials to cater to various industries.

Important Terms and Definitions

- *Composites are engineered materials,* comprising of metals, ceramics, glasses and polymers.
- *Natural composites are the materials occurring in mature* e.g. Wood or many other plant tissues contain cellulose chain polymer in a matrix of lignin. This is example of natural composite.
- *Synthetic composites* such as, rain proof cloth (cloth impregnated with waterproof material), packing paper impregnated with bitumen or wax, reinforced concrete, insulating tape are some examples.
- Thus composite may be defined as, "A multiphase product made by using two or more existing materials which exhibits properties of its constituents as well as shows certain unique properties of its own."
- Most of composites are made by using minimum two phases. The phases are namely :

  (a) Matrix

  (b) Dispersed phase.

  e.g. polymer composites in which matrix is of polymer and particles of metals/ceramic/fibre serves as dispersed phase.
- The polymer phase is called as *matrix* phase and the composite used for mixing is known as *dispersed phase.* The boundaries between the matrix and dispersed phase, are known as *inter phase.*

Review Questions

Q. 1 What are composites ? Give examples ?

Q. 2 Explain the role of composites in aviation industry.

Q. 3 Write a note on constitution of composites; giving suitable example.

Q. 4 Explain the term

(i) Matrix and

(ii) Dispersed Phase.

Q. 5 Name two types of composites based on dispersed phase.

Q. 6 List out ideal characteristics of matrix material

Q. 7 What are the main function of a matrix material in polymer composite ?

Q. 8 What are whiskers ? What are their special properties ? Give few examples.

Q. 9 List some important dispersed phase constituents. Discuss their features.

Q. 10 How are composites classified on the basis of reinforcing materials ?

Q. 11 Write notes on :

(i) Large particle reinforced composites.

(ii) Dispersion strengthened composites.

Q. 12 Which are the constituents of fibre reinforced composites ?

Q. 13 List out properties of fibre reinforced composites.

Q. 14 Which are the factors governing properties of fibre reinforced composites ?

Q. 15 Write notes on, giving phases, properties, use and limitations.

(a) Glass fibre reinforced polymer composites

(b) Carbon fibre reinforced polymer composites

(c) Aramid fibre reinforced polymer composites

(d) Alumina /carbon fibre reinforced polymer composites

Q. 16 Write a note on different "Layered composites."

Q. 17 Explain "Laminar composites" with suitable example.

Q. 18 Explain "Sandwich panel" with suitable example.

Q. 19 What are important application of composites ?

Q. 20 "Composites may be materials for future". Comment.

□□□

6

Green Chemistry

Syllabus

A) Comparative study of synthesis of following industrially important molecules by conventional and green route:- i) Indigo dye, ii) Adipic acid, iii) Carbaryl

B) Green Solvents : characteristics and applications of Supercritical solvents and ionic liquids

C) Green Fuels : Synthesis and Advantages of i) Biodiesel, ii) Ethanol.

6.1 Introduction

Q. What is Green chemistry? Give its significance. **May 18, 3 Marks**

- The *knowledge of chemistry* and all the developments in different branches of chemistry during last few decades have given many useful products to mankind, e.g. *medicines, fabrics, insecticides, drugs, dyes, rubber ,petrol, etc are few to mention.*
- The *dependence of humans* on all these formulations/products is *increasing*day by day and hence with growing populations *more* number of *industries* are established to produce *these products in large quantity.*
- The *chemical reactions* involved are always associated with certain *by-products* which are *harmful for the environment* and cause severe pollution problems.
- In fact all the *chemicals are toxic in varying extent.* Hence, to *minimize* the problems of *environmental pollution and hazardous waste* it became necessary to *review and modify* all the chemical processes used for manufacture .
- Thus design of harmless processes to produce various products has emerged as a new branch commonly known as "clean chemistry" or *"Green Chemistry" or "Environmentally benign chemistry".*
- *Green Chemistry* came into existence more than a decade back is now *becoming very popular.*
- It includes any chemical process or technology that improves the environment and thus our quality of life.
- Green chemistry is a highly *effective approach* to pollution prevention because it applies innovative scientific solutions to real-world environmental situations.
- The 12 Principles of Green Chemistry, originally suggested by *Paul Anastas and John Warner, are well accepted*by the chemists *all over the world.*

6.2 The Twelve Principles of Green Chemistry

Q. List and six principles of green chemistry. **May 17, 3 Marks**

1. Prevention of waste
2. Maximise Atom economy

3. Non-hazardous chemical
4. Safer chemical
5. Auxiliary Substances
6. Energy efficiency
7. Renewable feedstocks
8. Derivatisation
9. Catalysts
10. Degradable products
11. New Analytical methods
12. Accident prevention

We will discuss each of these principles in brief,

6.2.1 Prevention of Waste

Q. Explain the principle 'Prevention of waste' in green chemistry. Dec. 15, May 17, Dec. 17, 3 Marks

- "Prevention is better than the cure"
- It is better to prevent waste than to treat and clean up waste after it is formed.
- It has been a common practice to *dump* waste on land or in water or released in air. This resulted in soil, water and air pollution.
- This made the legislation to be stringent on industries and hence there was compulsion to have waste treatment and disposal units attached to the manufacturing plants. Thus the cost of process increased considerably.
- Thus green chemistry involves to design chemical syntheses in such a way that the process involves pathway to give products, leaving no waste to treat or clean up.

6.2.2 Maximize Atom Economy

- The design of the synthesis of the product should be such that all the chemicals/materials used in the process gets converted into the products to the maximum extent.
- It is common observation that most of the *organic reactions release undesired products* along with the useful products of the reaction.
- The unutilized material is considered as waste which causes trouble and the process becomes uneconomical.
- Green chemistry requires that new processes should be designed such that the most of the starting material gets converted into product. This is called as *Maximising atom economy.* This is explained further as ;

Atom Economy

- The theoretical yield for every reaction can be calculated as,

$$\text{Theoretical yield} = \text{Stoichiometric ratio} \times \left[\frac{\text{Molecular weight of the desired product}}{\text{Molecular weight of limiting reagent}}\right] \times \text{weight of limiting reagent}$$

- On conducting the reaction the experimental or actual yield of the process is obtained. From this percentage yield is calculated.

$$\text{Percentage yield} = \left[\frac{\text{Actual yield}}{\text{Theoritical yield}}\right] \times 100$$

e.g. Preparation of n-propyl bromide from n-propyl alcohol (0.6 g)

$$CH_3CH_2CH_2\text{-}OH + NaBr + H_2SO_4 \longrightarrow CH_3CH_2CH_2Br + NaHSO_4 + H_2O$$

Mol Wt = 60 103 98 Mol Wt. 123 120 18

Thus 1 mole of reactant gives one mole of product

Hence

$$\text{Theoretical yield} = \text{Stoichiometric ratio} \times \left[\frac{\text{Molecular weight of the desired product}}{\text{Molecular weight of limiting reagent}}\right] \times \text{Weight of limiting reagent}$$

$$= \frac{1}{1} \times \left[\frac{123}{60}\right] \times 0.6$$

$$= 1.23 \text{ gms}$$

But actually yield of the above reaction is found to be 0.99 gms

$$\text{Hence percentage yield} = \frac{0.99}{1.23} \times 100$$

$$= 80.49\ \%$$

Atom economy can be calculated by using following formula,

$$\%\ \text{Atom economy} = \frac{\text{Molecular weight of product}}{\text{Total molecular weight of reactants}} \times 100$$

∴ In above reaction, % atom economy can be calculated as,

$$\%\ \text{Atom economy} = \frac{\text{Molecular weight of n-propyl bromide}}{\text{Molecular weight of (n-propanol + NaBr)}} \times 100$$

$$= \frac{123}{60 + 103} \times 100$$

$$= \frac{123}{163} \times 100$$

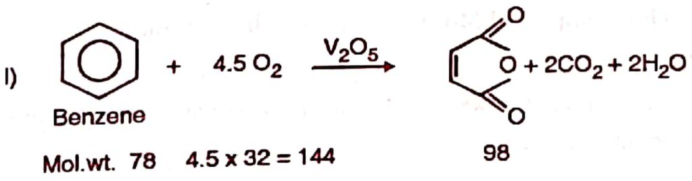
$$= 75.5\%$$

Other examples for understanding the efficiency of reaction is given here,

6.2.2(A) Preparation (synthesis) of Maleic Anhydride

- Maleic Anhydride can be prepared by oxidation of
  a) Benzene
  b) Butene
  c) Butane

I) $[C_4H_2O_3]$



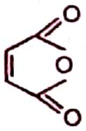
$$\%\ \text{Atom economy} = \frac{98}{78 + 144} \times 100$$

$$= \frac{98}{222} \times 100$$

$$\therefore\ \%\ \text{Atom economy} = 44.1\%$$

II) $[C_4H_2O_3]$

$C_4H_8 \quad + \quad 3O_2 \longrightarrow$



$+ 3H_2O$

Butene

Mol. Wt. = 56 $\quad 3 \times 32 = 96 \quad$ 98

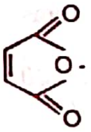
$$\text{\% Atom economy} = \frac{98}{56+96} \times 100$$

$$= \frac{98}{152} \times 100$$

∴ % Atom economy = 64.5 %

III) $[C_4H_2O_3]$

$C_4H_{10} \quad + \quad 2.5\ O_2 \longrightarrow$



$+ \quad 4H_2O$

Butane

Mol. wt. = 58 $\quad 2.5 \times 32 = 80 \quad$ 98

$$\text{\% Atom economy} = \frac{98}{58+80} \times 100$$

$$= \frac{98}{138} \times 100$$

∴ % Atom economy = 71.0 %

- Thus for different reaction atom economy can be calculated and thus the process giving maximum atom economy can be selected.
- The processes with *90 % yield* and *higher atom* economy are considered as *excellent* and those with *20 % yield* and *lower atom economy* are *poor.*
- Thus it becomes essential to design synthesis so that the final product contains the maximum proportion of the desired product thereby increasing the atom economy. There should be few, if any, wasted atoms.

6.2.3 Non-hazardous Chemical Synthesis

- The synthetic method should be designed wherever possible to use and generate substances having little or no toxicity to human health and the environment.
- The starting material selected should be least toxic. Thus e.g. pyridine, or β-naphthyl amine being known to be carcinogenic should be avoided as starting materials.
- The reactions in which intermediates or reagents or products are toxic, should not be followed. In stead alternative pathways should be used for synthesis.
- For example : In 1984, due to leakage of MIC at Bhopal there was major casualty and the after effects of the same are still suffered by many. This compound MIC is an intermediate in manufacture of agricultural pesticides and was known to be highly poisonous.
- Hence green chemistry recommends the design of synthesis to use and generate substances with little or no toxicity to humans and the environment.
- Other example is of synthesis of indigo as given below.

6.2.4 Design Safer Chemicals and Products

- The chemical products should be designed to preserve the efficiency of desired function while reducing toxicity.
- When any medicinal formulations are to be put in market, they are put first on trials to check their toxic effects on humans.

- If found to be toxic then alternatives are prepared keeping in mind the function of the medicine but only toxicity reduced.
- Similarly in many insecticides like *DDT, gamaxane, aldrin*etc which are found to be *toxic to humans*, the use of these is *curtailed* and alternatively *biological pesticides* are more in use.
- Thus green chemistry emphasizes to design chemical products to be fully effective, yet have little or no toxicity.

6.2.5 Auxiliary Substances (Use Safer Solvents and Reaction Conditions)

- The use of auxiliary substances like solvents, separating agents etc. should be made unnecessary wherever possible and innocuous when used.
- Avoid using carcinogenic solvents, separation agents, or other auxiliary chemicals. If these chemicals are necessary, use innocuous chemicals.
- The solvents such as **acetone, benzene, ether** being highly inflammable should be *avoided.*
- Other chemicals such as CCl_4, $CHCl_3$,carry health risk hence should be *avoided.*
- If a solvent is necessary, *water is a good medium* as well as certain *eco-friendly solvents* that do not contribute to smog formation or destroy the ozone.
- **For example :** For *drycleaning*the fabrics, the toxic solvent like *perchloroethylene* was used, which is *replaced* during recent years by*liquid* CO_2.

6.2.6 Energy Efficiency

Q. Explain 'Design for Energy Efficiency' principle of Green Chemistry. **Dec. 18, 3 Marks**

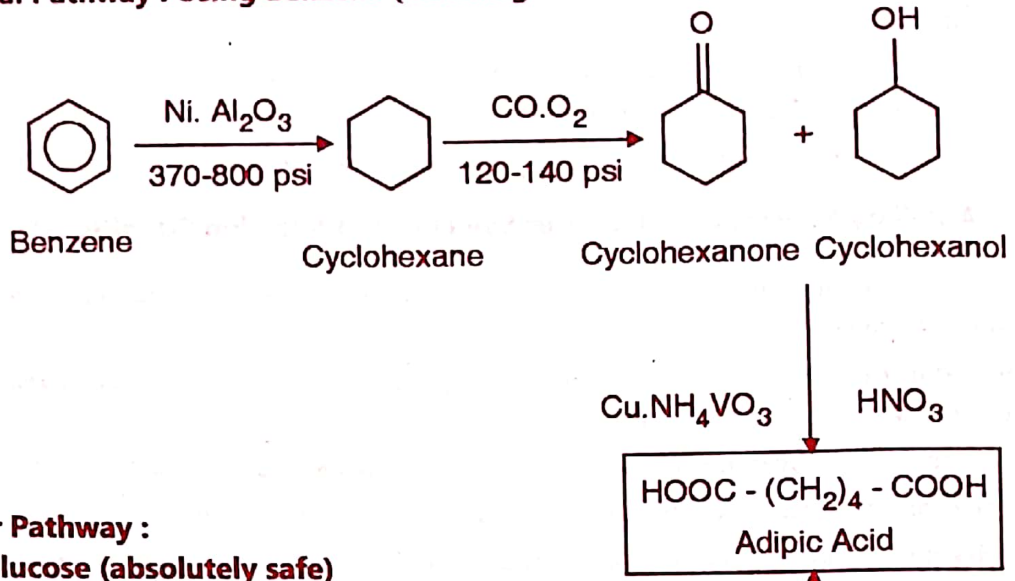
- The energy requirements of chemical processes should be minimized considering their environmental and economic impacts. The synthetic methods should be carried out at ambient temperature and pressure wherever possible.
- The aim of green chemistry is to increase energy efficiency.
- This can be achieved by use of catalysts, and by stopping the use of fossil / gaseous fuels which release solid or gaseous pollutants.
- The recently found substitutes are microwave radiations and ultra sound, which are used in the processes requiring very less energy.
- The energy efficiency of process can be increased by
  a) proper heat transfer and
  b) minimal wastage of energy during the process.
- Many chemical are produced by *fermentation* process where energy requirement is low and also the products are less harmful

6.2.7 Use Renewable Feedstock (Waste Utilisation)

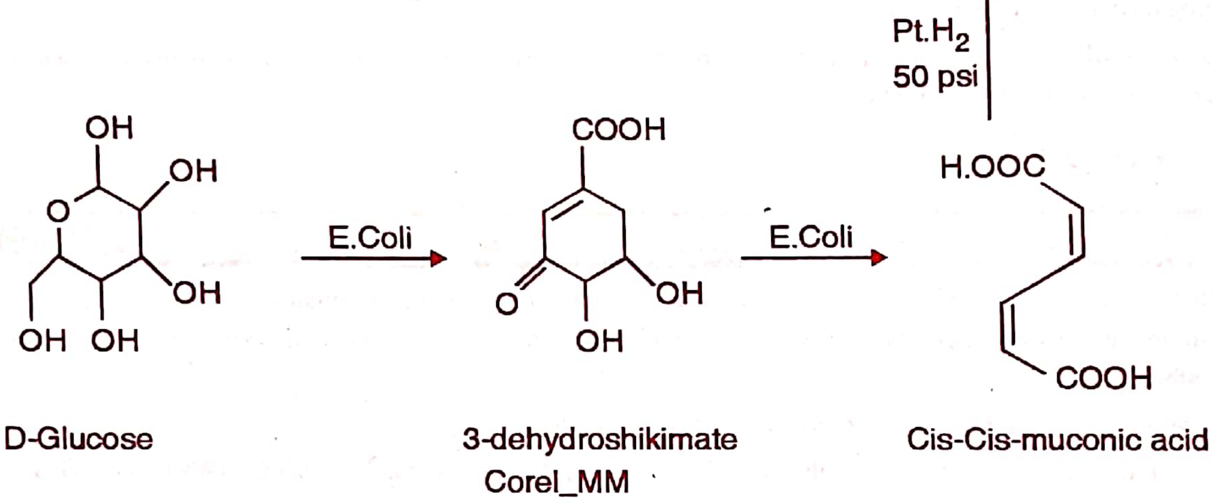
- The raw materials should be renewable rather than depleting, wherever technically and economically feasible.
- Renewable feedstock are often made from agricultural products or are the wastes of other processes; depleting feedstock are made from fossil fuels (petroleum, natural gas, or coal) or are mined.
- For example : A new method is developed to prepare adipic acid from glucose obtained from corn starch or cellulose. This is green process because it *replaces benzene* as starting material for production of same product. *Benzene* is a known *carcinogen.*

Synthesis of Adipic Acid

6.2.7(A) Traditional Pathway : Using Benzene (Carcinogenic Solvent)



6.2.7 (B) Greener Pathway : Using Glucose (absolutely safe)



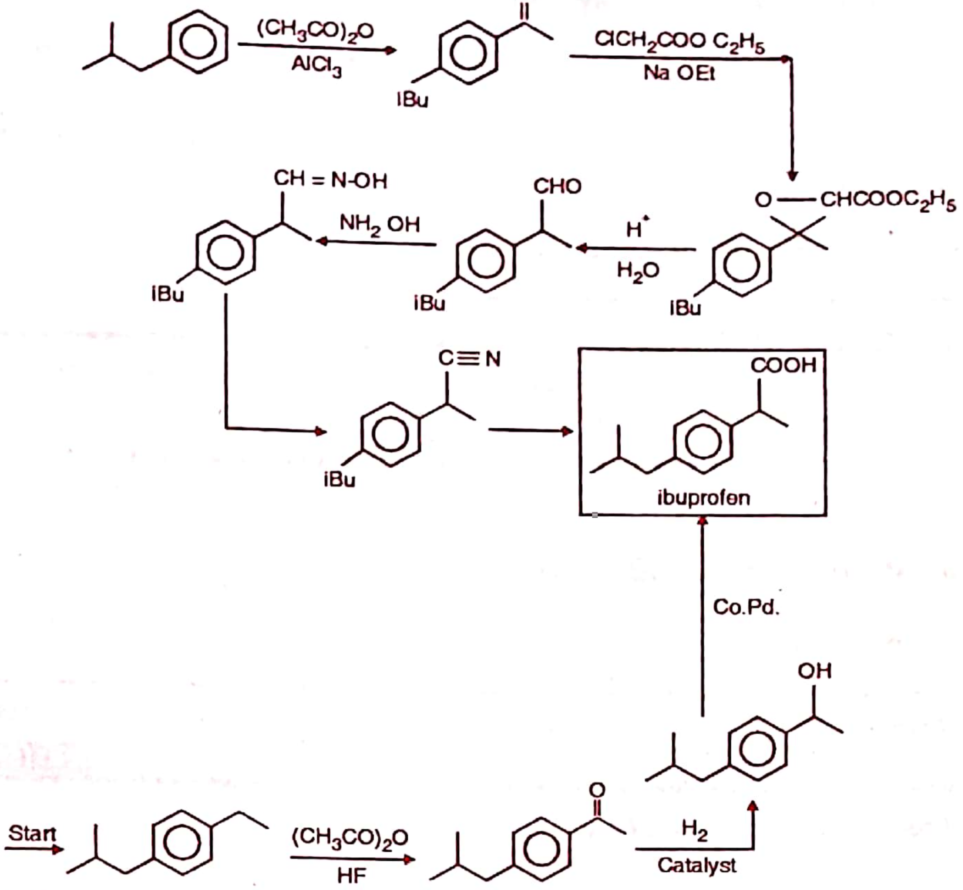
6.2.8 Avoid Chemical Derivatives

- During synthesis unnecessary derivatisation such as blocking or protecting groups or any temporary modifications should be avoided, if possible.
- The use of derivatives *increases the steps* of the process.
- The additional reagents are required.
- It generates more waste products.
- To avoid these effects, alternative reagents are to be used which are more *selective*.
- **Example :** *Synthesis of Ibuprofen* is given below where in traditional pathway larger number of steps are involved, and atom economy is low. This has been modified to increase atom economy.

Synthesis of Ibuprofen

(A) Traditional method

With larger number of steps (Atom economy = 40 %)



(B) Alternative Synthesis

With the atom economy = 77 % and recoverable catalyst.

6.2.9 Use Catalysts, not Stoichiometric Reagents

- The catalytic reagents which are selective in their reaction, are preferred over stoichiometric reagents.
- Minimize waste by using *catalytic reactions.*
- *Catalysts* are used in small amounts and can carry out a single reaction *many times.*
- They are preferable to *stoichiometric reagents,*which are used in excess and work *only once.*
- Catalytic *reactions are faster* and hence require less energy.
- In recent years many processes are been developed which use *non toxic recoverable catalysts and also biocatalysis.*

6.2.10 Design Chemicals and Products to Degrade after use

Chemical products should be designed such that they break down to innocuous substances after use so that they do not accumulate in the environment.

Examples

1. *DDT* when used as pesticide, its residues remain in *soil* for many years causing *pollution.* The *alternative* to this is *biological insecticides.*
2. The packaging material such as plastics or polystyrene are non biodegradable and cause solid waste. The alternative to this the *biodegradable plastics containing cellulose* and the packing pellets made up of starch are used.

6.2.11 New Analytical Methods : (Analyze in Real Time to Prevent Pollution)

- New analytical processes have to be developed to allow on-line monitoring and control prior to the formation of hazardous substances.
- **Example :** *Preparation of ethylene glycol*, in which if reaction conditions are not monitored perfectly, toxic substances are produced at higher temperature.

6.2.12 Minimize the Potential for Accidents

Q. Explain the principle "Inherently Safer Chemistry of Accident Prevention" in green chemistry. **May 19, 3 Marks**

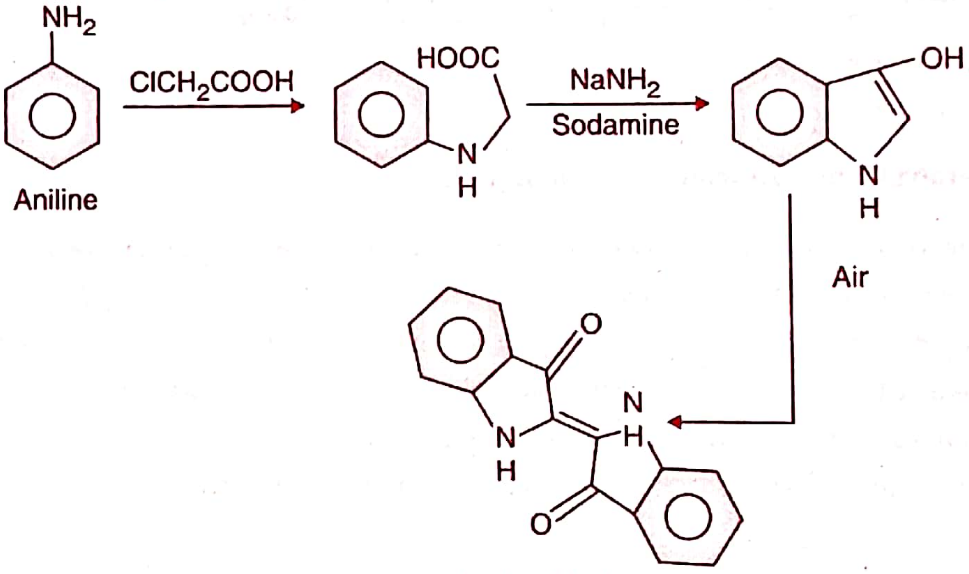
- The substances and its forms used in chemical process should be chosen to minimize the potential for the chemical releases, accidents, explosions and fire.
- The use of safer chemicals, minimizing temperature, pressure and using catalysts helps in minimizing the potential of accidents which is desirable.

6.3 Synthesis of Adipic Acid and Indigo

6.3.1 Synthesis of Indigo

Q. Explain conventional and green synthesis of Indigo dye. Mention the green chemistry principle involved. **Dec. 15, May 16, 5 Marks**

1. **Conventional route using hazardous Aniline**

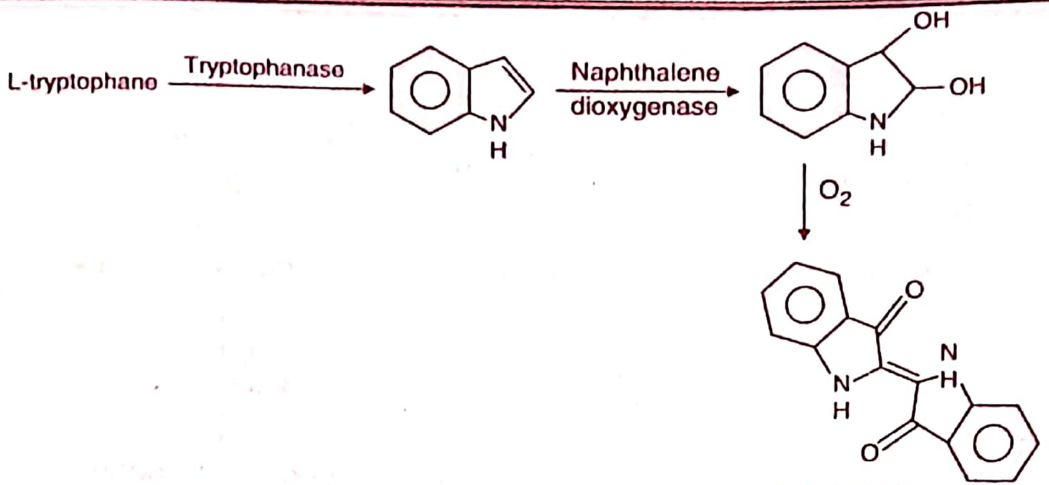


Indigo (dye)

- In conventional method, aniline is treated with chloroacetic acid and the resultant heterocyclic carboxylic acid which is treated with sodamine to get a heterocyclic phenol.
- This is followed by coupling reaction in air to result in cyclisation forming indigo dye.

2. **Green route using enzyme**

- Greener route involves enzyme reaction starting with L-tryptophane treated with tryptophase to get heterocyclic compound, which is treated with naphthalene in dioxygenase to get a heterocyclic di-phenol which is oxygenated to form indigo dye.



The above example is to meet with green chemistry principle of "Avoid use of hazardous chemicals".

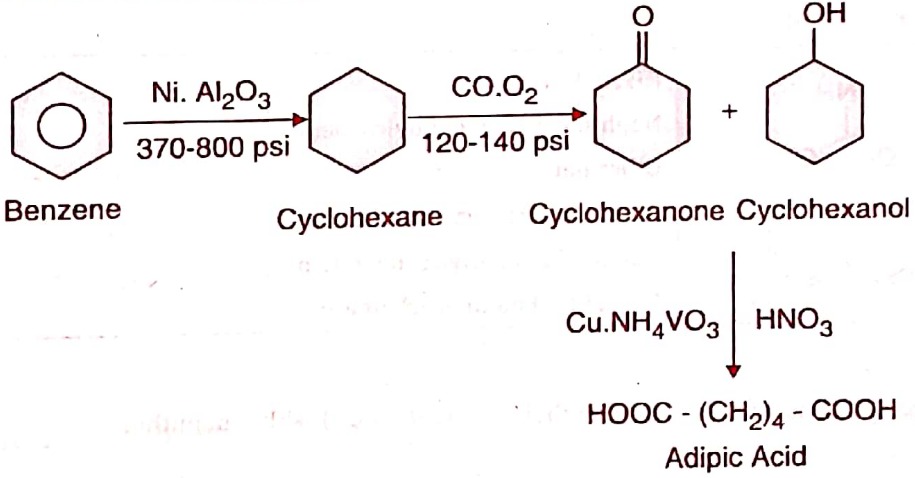
6.3.2 Synthesis of Adipic Acid

Q. Explain conventional and green synthesis of adipic acid. Mention the green chemistry principle involved.
May 15, 5 Marks

Q. Explain conventional and green route of manufacturing of Adipic acid.
May 17, May 19, 4 Marks

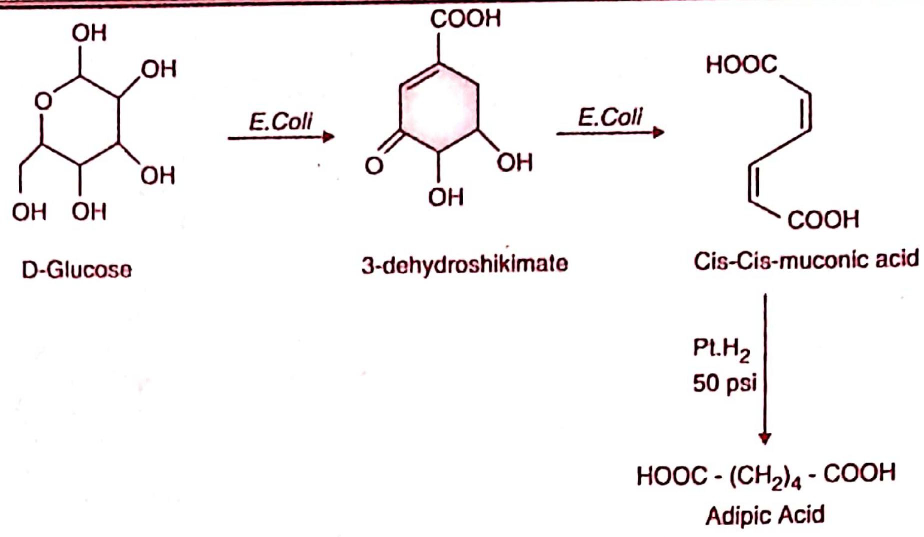
1. Conventional route using Benzene (Carcinogenic solvent)

- For synthesizing adipic acid molecule, starting material is benzene, treated with Ni/alumina catalyst at high pressure to get a saturated cyclic hydrocarbon, cyclohexane.
- This is treated with carbon monoxide in presence of oxygen at medium pressure to get mixture of cyclohexanone and cyclohexanol as intermediate which are converted into adipic acid.



2. Green route using glucose (absolutely safe)

- To get adipic acid by green route, starting material is D glucose, which is simply fed with E. Coli in specified dose to get 3-dehydroshikimate as first intermediate, cis-cis muconic acid as second intermediate. Further it is catalytically with Pt.-hydrogen catalyst at pressure 50 psi to give adipic acid.
- This route is inexpensive, fast with high atom economy.
- This is example of avoid hazardous chemicals and also avoid derivatization.



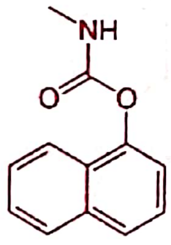
6.3.3 Carbaryl (1-naphthyl methylcarbamate)

- It is a chemical from the carbamate family.
- It is mainly used as an insecticide.
- Colour & texture : It is a white crystalline solid It was popularly known as Sevin, (a trademark of the **Bayer** Company).

History :

- Originally the Union Carbide discovered carbaryl and introduced it commercially in 1958.
- Bayer purchased Aventis CropScience in 2002, a company that included Union Carbide pesticide operations.
- The GardenTech took over this trademark, and then modified the formulation by removing carbaryl to make it safer to use.

Structure and nomenclature

	IUPAC Name Naphthalen-1-yl methylcarbamate Other names Sevin (Generic trademark) Naphthyl N-methylcarbamate or 1-Naphthyl methylcarbamate

Preparation

Carbaryl is prepared by direct reaction of methyl isocyanate (MIC) with 1-naphthol.

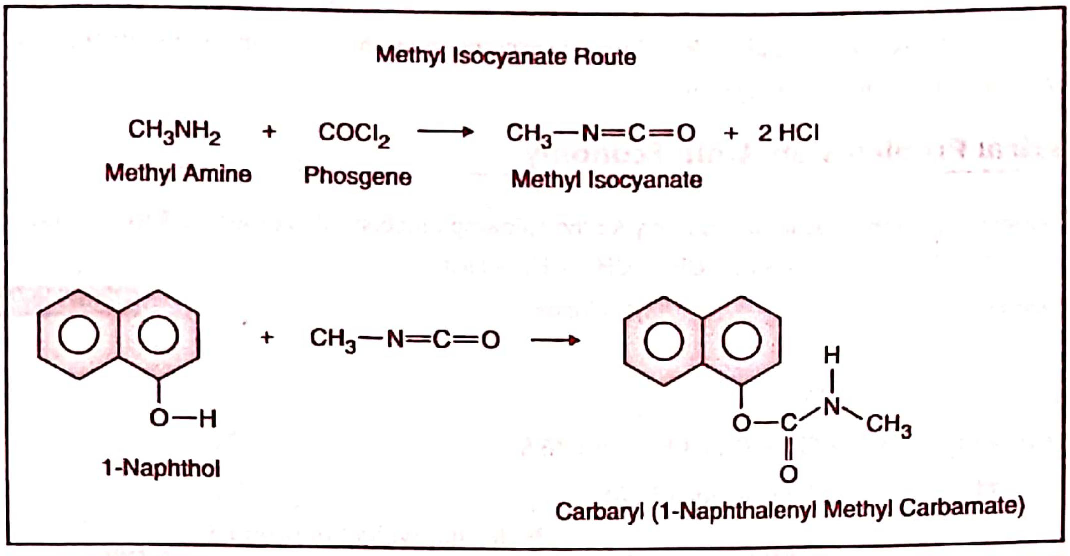
Reaction

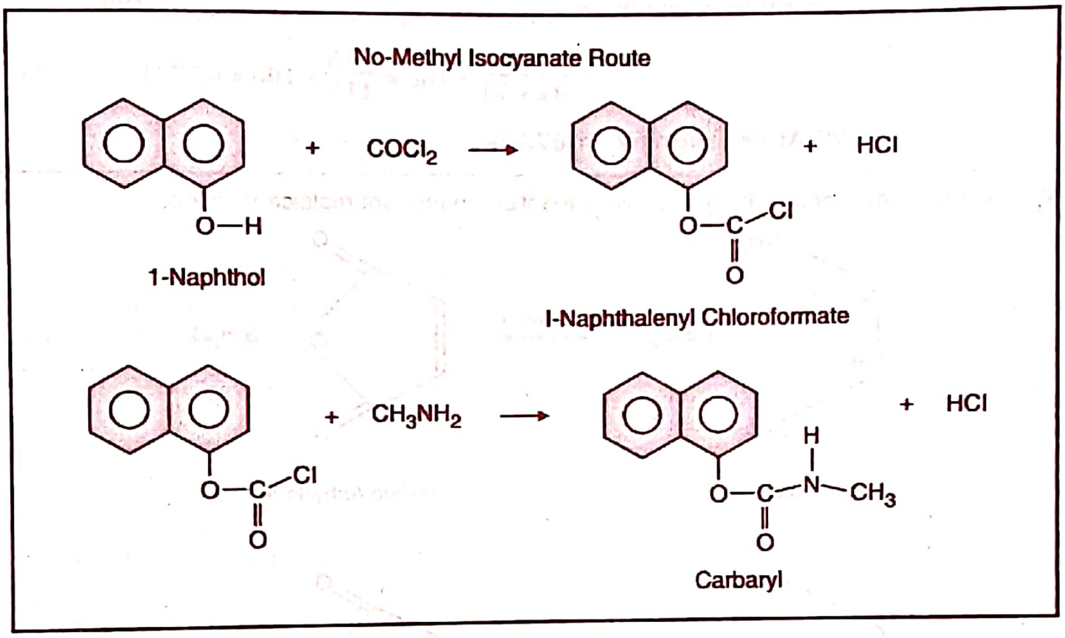
$C_{10}H_7OH + CH_3NCO \rightarrow C_{10}H_7OC(O)NHCH_3$

- This process was carried out in Bhopal, by Union Carbide company. A leak of MIC used in the production of carbaryl caused the Bhopal disaster, the most lethal industrial accident in history.
- Considering the hazards of MIC,the alternate synthesis brought in practice, which uses exactly the same reagents, but in a different sequence. This procedure avoids the potential hazards of methyl isocyanate.
- Alternatively, A safer two step process is followed as;

Step 1 : 1-naphthol + excess phosgene → 1-naphthylchloroformate,

Step 2 : 1-naphthylchloroformate + Methylamine →carbaryl





Biochemistry / action

Carbamate insecticides when inhaled by pests, it interferes with the cholinergic nervous system and cause death of the pests.

Applications

- These chemicals made a major breakthrough in **"pesticides"** over the usual chlorinated compounds used before.
- The carbamates are better than the chlorinated pesticides, as they do not persist.
- Carbaryls are, though toxic to insects, they get detoxified and eliminated quickly in vertebrates.
- Carbaryls are neither concentrated in fat nor secreted in milk, so is favoured for food crops.
- Used also for killing lice in hair, as shampoo

Disadvantages

Carbaryl kills both harmful and beneficial insects (e.g., honeybees), and harms aquatic species in long term use.

Safety

Carbaryl is toxic and It is classified as a likely human carcinogen by the Environmental Protection Agency (EPA.). It is used to kill rats and mice, but needs precaution.

6.4 Numerical Problems on Atom Economy

Ex. 6.4.1 : Calculate the percentage atom economy for the following reaction with respect to Allyl chloride.

$$CH_3 - CH = CH_2 + Cl_2 \longrightarrow Cl - CH_2 - CH = CH_2 + HCl$$

Propene Allyl chloride

Dec. 18, May 19, 4 Marks

Soln. :

Reaction given :

$$CH_3 - CH = CH_2 + Cl_2 \longrightarrow Cl - CH_2 - CH = CH_2 + HCl\ 36.5$$

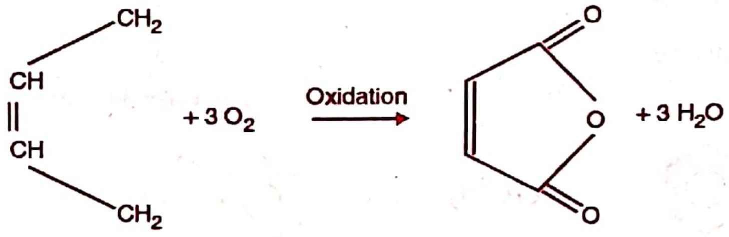
Propene 42 71 Allyl chloride (76.5)

$$\%\ \text{Atom economy} = \frac{\text{Molecular weight of product}}{\text{Total molecular wt. of reactants}} \times 100$$

$$= \frac{76.5}{42 + 71} \times 100 = \frac{76.5}{113} \times 100 = 67.7\ \%$$

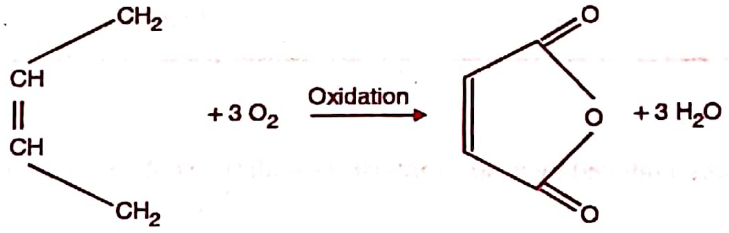
% Atom economy = 67.7% ...**Ans.**

Ex.6.4.2 : Calculate the atom economy for the following reaction, to prepare maleicanhydride.



2 – Butene Maleic Anhydride

Soln. :



2 – Butene
mol.wt. = 56 3 × 32 = 96

Maleic Anhydride
mol. wt. = 98

$$\%\ \text{Atom economy} = \frac{\text{Molecular weight of product}}{\text{Total molecular weight of reactants}} \times 100$$

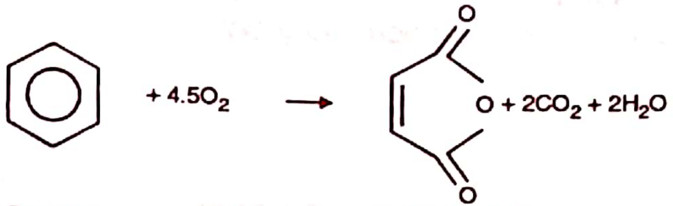
$$= \frac{98}{56 + 96} \times 100$$

$$= \frac{98}{152} \times 100$$

$$= 64.5\ \%$$

% Atom economy = 64.5% ...**Ans.**

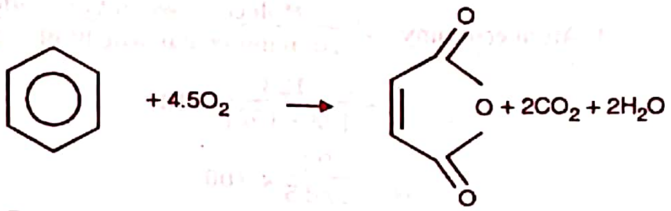
Ex. 6.4.3 : Calculate the atom economy for the following reaction.



Benzene Maleic Anhydride

Soln. :

Given data :



Benzene Maleic Anhydride

Mol. wt. 78 $4.5 \times 32 = 144$ 98

$$\therefore \text{\% Atom economy} = \frac{98}{78+144} \times 100$$

$$= \frac{98}{222} \times 100 = \mathbf{44.1\ \%}$$

% Atom economy = 44.1% **...Ans.**

Ex.6.4.4 : Calculate the percent atom economy for the following reactions –

(i) $CH_3CH = CH_2 + H_2 \xrightarrow{Ni} CH_3CH_2CH_3.$

(ii) $C_6H_6 + CH_3Cl \xrightarrow{AlCl_3} C_6H_5CH_3 + HCl.$

Soln. :

(i) $CH_3CH = CH_2 + H_2 \xrightarrow{Ni} CH_3CH_2CH_3.$

Molecular weight = 42 2 44

$$\text{\% Atom economy} = \frac{\text{Molecular weight of product}}{\text{Total molecular weight of reactants}} \times 100$$

$$= \frac{44}{42+2} \times 100$$

$$= \frac{44}{44} \times 100 = 100\ \%$$

(ii) $C_6H_6 + CH_3Cl \xrightarrow{AlCl_3} C_6H_5CH_3 + HCl.$

Molecular weight = 78 50.5 92

$$\text{\% Atom economy} = \frac{\text{Molecular weight of product}}{\text{Total molecular weight of reactants}} \times 100$$

$$= \frac{92}{78+50.5} \times 100$$

$$= \frac{92}{128.5} \times 100$$

$$= 71.5\%$$

% Atom economy = (i) 100% (ii) 71.5% **...Ans.**

Ex. 6.4.5 : Calculate the percentage atom economy for the following reaction with respect to acetanilide :

$C_6H_5NH_2 + (CH_3CO)_2O \longrightarrow C_6H_5NHCOCH_3 + CH_3COOH.$

Acetanilide

Soln. :

Reaction given :

$$C_6H_5NH_2 + (CH_3CO)_2O \longrightarrow C_6H_5NHCOCH_3 + CH_3COOH.$$

	Aniline	Acetic Anhydride	Acetanilide	Acidic acid
Mol. wt. =	93	102	92	123

$$\% \text{ Atom economy} = \frac{\text{Molecular weight of product}}{\text{Total molecular weight of reactants}} \times 100$$

$$= \frac{123}{(93+102)} \times 100$$

$$= \frac{92}{128.5} \times 100$$

$$= 51.5\%$$

$$= \frac{123}{195} \times 100$$

$$= 63.07\,\%$$

$$\textbf{\% Atom economy} = \textbf{63.07 \%}$$ **...Ans.**

Ex. 6.4.6 : Calculate the atom economy of the following reaction.

$$C_6H_6 + 4\cdot 5O_2 \xrightarrow{V_2O_5} C_4H_2O_3 + 2CO_2 + 2H_2O$$

Soln. :

$$C_6H_6 + \quad 4.5\,O_2 \xrightarrow{V_2O_5} C_4H_2O_3 \quad + 2CO_2 + 2\,H_2O$$

Benzene 4.5 × 32

Mol. Weight 78 = 144

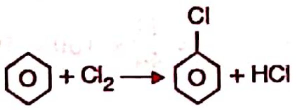
Maleic

Anhydride

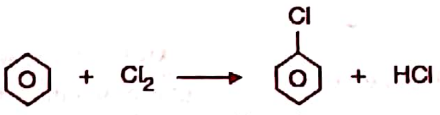
Mol. Weight 98.

(Refer to example 6.4.3 for solution.)

Ex. 6.4.7 : Calculate % atom economy for following reactions :



Soln. :



Benzene	Chlorine	Chlorobenzene
Mol.wt = 78	71	112.5

$$\% \text{ Alom Economy} = \frac{\text{Mol. Weight of product}}{\text{Total molecular weight of reactants}} \times 100$$

$$= \frac{112.5}{78+71} \times 100$$

$$= \mathbf{75.5\,\%}$$ **...Ans.**

Ex. 6.4.8 : Calculate percentage atom economy for the following reaction with respect to acetophenone :

$$\underset{\text{Benzene}}{C_6H_6} + CH_3COCl \xrightarrow{AlCl_3} \underset{\text{acetophenone}}{C_6H_5COCH_3} + HCl$$

May 18, 4 Marks

Soln. :

$$\underset{\text{Benzene}}{C_6H_6} + CH_3COCl \xrightarrow{AlCl_3} \underset{\text{Acetophenone}}{C_6H_5COCl} + HC1$$

Mol. wt. = 78 78.5 140.5

To Calculate % atom economy for reaction,

$$\% \text{ Atom Economy} = \frac{\text{Weight of product}}{\text{Total weight of Reactants}} \times 100$$

$$= \frac{140.5}{78 + 78.5} \times 100$$

$$= 89.78 \%$$

...Ans.

6.5 Green Solvents

The "Green solvents" – a newer concept involves the technology which has been popularly preferred over conventional solvent extraction process because of environmental concerns, such as the need to eliminate organic solvents and to find appropriate technologies for their disposal. e.g. Ionic liquid CO_2, propylene Glycol etc.

6.5.1 Ionic Liquid Supercritical CO_2

- Supercritical fluids (SCFs)possess properties of gases and liquids in an intriguing manner, which could offer a range of applications / possibilities in both synthetic and analytical chemistry.
- Supercritical / Ionic liquid carbon dioxide has found to be an energy conserving, selective and waste reducing alternatives to organic solvents and therefore is viewed as promising environmentally benign solvents. In addition, supercritical fluids can lead to reaction, which are difficult or even impossible to achieve in conventional solvents.
- Supercritical / Ionic liquid extraction is relatively new technology with a large potential for application in industry.

Among the many advantageous qualities of ILs are:

- Low melting point : Many ILs melt at room temperature or even below 0 °C.
- ILs have a melting point of less than 100 °C.
- Low vapour pressure : It is simple to purify ILs due to their extremely low vapour pressure.
- Inflammability : ILs don't catch fire.
- Thermal stability : The thermal stability of ILs is very high. Electrochemical stability: The electrochemical stability of ILs is very high.

Principle

- The basic principle of Supercritical Fluid Extraction (SFE) technology is that when the *feed material is contacted* with a *supercritical fluid* then the *volatile substances* will *partition* into the *supercritical phase.*
- After the dissolution of soluble material the supercritical fluid containing the dissolved substances is removed from the feed material.

- The extracted component is then completely separated from the supercritical fluids (SCF) by means of a temperature and/or pressure change. The SCF may then be recompressed to the extraction conditions and recycled.

Choice of Solvents of Supercritical fluid Extraction

- The choice of the SFE solvents is similar to a regular extraction. Principal considerations are as follow :
    - Good solvent property
    - Inert to the product
    - Easy separation from the product
    - Low cost
- *Carbon dioxide* is the most commonly used *SCF*, primarily due to its low critical parameters (31.1°C, 73.8 bar), low cost and non-toxicity. However, several other SCF's have also been used in industrial processes.

Applications of SCFs:

- Plant extracts, antioxidants, and floral scents can all be extracted using SCFs.
- Decaffeination : Coffee is decaffeinated using SCFs.
- Food science : SCFs have applications in this field.
- Pharmaceuticals : SCFs can be used to examine chemical compounds in drugs, as well as herbicides and insecticides.
- Cosmetics : Antioxidants from fruits and vegetables can be extracted using SCFs.
- Polymers and plastics : SCFs can be used to modify polymer structures.
- Textiles : Tan leather and textiles can be dyed with SCFs.
- Petroleum : Total aromatic content and other hydrocarbon separations can be exam

Applications of Ionic Liquids (ILs)

- ILs are employed in electrolytes as redox species or solvents, such as:
- Reactions: In chemical reactions, ILs are employed as environmentally friendly solvents.
- Functional materials: The production of functional materials involves the usage of ILs.
- Processes catalysed by transition metals: ILs are useful solvents for these processes because they dissolve organometallic compounds.

6.6 Green Fuels

Green fuels, or synthetic or electrofuels (e-fuels), are either liquids or in gaseous form which are obtained from renewables using electricity preferably solar or wind.

Characteristics

These are carbon-neutral i.e. when are burned, they emit only the amount of CO_2 which can be absorbed during its production

Advantages

1. They have very low or negative carbon footprints.
2. These are renewables.
3. Environment pollution is reduced

Disadvantages

1. Production cost and resourcesis high.

Examples:

1. synthetic natural gas (SNG),
2. green methanol or ammonia.
3. Renewable gasoline/ green gasoline
4. Ethanol.
5. Biodiesel

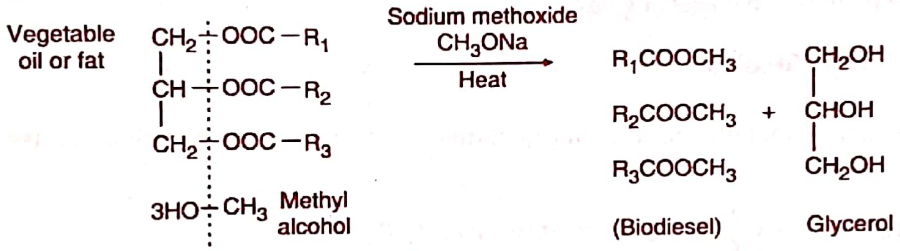
6.6.1 Production of Biodiesel (By Trans-esterification)

Chemical nature : Chemically biodiesel is *the methyl esters of long chain carboxylic acids.* Biodiesel is obtained by transesterification of vegetable oil or animal fats with methyl alcohol using sodium metal or sodium methoxide, as catalyst.

Transesterification

- Transesterification is the process of converting one ester to another ester.
- A molecule of oil or fat is the triester of glycerol and three molecules of long chain carboxylic acids. This triester is converted into methyl esters of the fatty acids.

Reaction :-



- During the chemical conversion of vegetable oil to biodiesel we get water soluble glycerol and a small amount of sodium soaps.
- The water soluble part can be easily separated from biodiesel by washing the mixture with water.
- The alkaline sodium methoxide catalyst, saponifies some small amount of oil to give soap.
- Compounds present in biodiesel are like,

methyl palmitate	$H_3C-(CH_2)_{14}-COOCH_3$
methyl stearate	$H_3C-(CH_2)_{16}-COOCH_3$
methyloleate	$H_3C-(CH_2)_7-CH=CH-(CH_2)_7-COOCH_3$
methyl linoleate	$H_3C-(CH_2)_5(CH=CH_2)-(CH_2)_7-COOCH_3$

6.6.1(A) Method / Steps to obtain Biodiesel – A Green Fuel

i) Filter the cheap or waste vegetable oil / fat.

ii) Heat it at 110° C with stirring to remove any water from it.

iii) Prepare sodium methoxide from sodium metal and methanol. Add the sodium methoxide about 2% by weight to the vegetable oil or fat.

iv) Add methanol about 20% by volume to the mixture.

v) Heat the mixture with stirring for 30 minutes.

vi) Cool and mix sufficient water, stir well. The glycerol and soap dissolve in water phase.

vii) Separate the water insoluble phase (biodiesel) from water phase.

viii) Add antioxidant to the biodiesel to avoid it to become gummy due to oxidation and polymerisation.

- Biodiesel can be obtained from various vegetable oils like soyabeen oil, palm oil, groundnut oil, cottonseed oil, musturd oil, sunflower oil etc. and also from animal fats.
- The product is given name 'biodiesel' on account of that it is obtained from biological product and it is *biodegradable material*or Green Fuel.

6.6.1(B) Advantages of Biodiesel

Biodiesel can be used as a good fuel for diesel engines but generally it is used as its 20% mixture with diesel.

i) Biodiesel is cheaper.

ii) It has high cetane numbers*46 to 54* and high C.V. of about 40 kJ/gm.

iii) It is regenerative and environment friendly.

iv) It does not give out particulate and CO pollutants.

v) It has certain extent of *lubricity.*

vi) Its use provides good market to vegetable oils and reduces our dependence for diesel on foreign countries, saving currency.

vii) It is clean to use biodiesel in diesel engines.

6.6.2 Ethanol/Ethyl Alcohol

- Ethyl alcohol is mainly manufactured by fermentation of molasses, starch, carbohydrates on a large scale and cheaply.

$$\underset{\text{starch}}{(C_6H_{10}O_5)_n} + \frac{n}{2}H_2O \xrightarrow[\text{enzyme}]{\text{diastase}} \underset{\text{maltose}}{\frac{n}{2}C_{12}H_{22}O_{11}} \xrightarrow{\text{maltase}} \underset{\text{glucose}}{n\,C_6H_{12}O_6}$$

$$\underset{\text{sucrose in molasses}}{C_{12}H_{22}O_{11}} \xrightarrow[H_2O]{\text{invertase}} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

$$\underset{\text{glucose/fructose}}{C_6H_{12}O_6} \xrightarrow{\text{Zymase}} 2\,C_2H_5OH + 2\,CO_2$$

- The starch or sucrose in molasses is converted into ethyl alcohol by fermentation as in above reactions. The ethyl alcohol obtained contains 95.5 % alcohol and 4.5% water. This 4.5% water from ethyl alcohol is separated either by use of suitable dehydrating agent or by distilling it alongwith benzene.
- Thus it gives boost to the indigenous manufacturers of ethyl alcohol and farmers get better price of their grains produce.
- When ethyl alcohol is used as fuel in internal combustion engine, it is called as power alcohol. Generally, ethyl alcohol is used as its 5-25% mixture with petrol.
- India has started mixing 5% ethyl alcohol in petrol from year 2003, but countries like Brazil use 25% ethyl alcohol in petrol from 1970.
- Use of ethyl alcohol in petrol reduces our dependence for petrol on foreign countries and even 5% ethyl alcohol blending in petrol, saves our foreign reserves by about Rs. 5000 crores/annum

6.6.2(A) Advantages of Alcohol

i) Ethyl alcohol has good antiknocking property and its octane number is 90, while the octane number of petrol is about 65. Therefore addition of ethyl alcohol to petrol, increases its octane number.

ii) Alcohol has property of absorbing any traces of water if present in petrol.

iii) If a specially designed engine with higher compression ratio is used, then the disadvantage of lower C.V. of ethyl alcohol can be overcome.

iv) Ethyl alcohol contains 'O' atoms, which help for complete combustion of power alcohol and the polluting emissions of CO, hydrocarbon, particulates are reduced largely.

v) Use of ethyl alcohol in petrol reduces our dependence on foreign countries for petrol and saves foreign currency considerably.

vi) Power alcohol is cheaper than petrol.

6.6.2(B) Disadvantages of Power Alcohol

i) Ethyl alcohol has C.V. 7000 cal/gm, much lower than C.V. of petrol 11500 cal/gm. Use of power alcohol reduces power output upto 35%.

ii) Ethyl alcohol has high surface tension and its atomisation, especially at lower temperatures is difficult causing starting trouble.

iii) Ethyl alcohol may undergo oxidation to form acetic acid, which corrodes engine parts.

iv) Ethyl alcohol obtained by fermentation process directly cannot be mixed with petrol but it has to be dehydrated first.

v) As ethyl alcohol contains 'O' atoms, the amount of air required for complete combustion of power alcohol is lesser and therefore carburettor needs to be adjusted / modified.

6.7 Products from Natural Materials

The biodiversity of plants and microbes is an unending resource for newer chemical templets. It provides information on the synergy of molecular tools like *genomics, proteomics* and *advanced bioanalytical technique* for development of new drugs or new molecules.

Plants as a Sources of New Drugs/Biomolecules

- Plants have been playing an important role in the field of pharmacy, not only in ancient times but also in the arena of modern drug discovery.
- The chemical diversity of plants gives the important clew for synthesis of different efficient pharmacophores in pharmaceutical drug design.
- Examples like Mepridine (Demerol), Pentazocine (Darvon), are totally synthetic drugs for which opiates such as morphine and codeine were the models.
- Japanese research group has recently isolated Stilbene derivative from the bark of a *Shoreahemsleyana* (dipterocarpeaceae) and roots of Cyphostemmabainessi (Vitaceae).
- The active compound identified is Hemsleyanol-D is a potent antibacterial agent Methicillin resistant staphylococcus aureus (MRSA) responsible for variety of human diseases.

Important Terms and Definitions

- The design of harmless processes to produce various products has emerged as a new branch commonly known as "clean chemistry" or *"Green Chemistry" or "Environmentally benign chemistry".*
- Atom economy can be calculated by using following formula,

$$\% \text{ Atom economy} = \frac{\text{Molecular weight of product}}{\text{Total molecular weight of reactants}} \times 100$$

- In conventional method, aniline is treated with chloroacetic acid and the resultant heterocyclic carboxylic acid which is treated with sodamine to get a heterocyclic phenol.
- Greener route involves enzyme reaction starting with L-tryptophane treated with tryptophase to get heterocyclic compound, which is treated with naphthalene in dioxygenase to get a heterocyclic di-phenol which is oxygenated to form indigo dye.
- The "Green solvents" – a newer concept involves the technology which has been popularly preferred over conventional solvent extraction process because of environmental concerns, such as the need to eliminate organic solvents and to find appropriate technologies for their disposal. e.g. Ionic liquid CO_2, propylene Glycol etc.
- **Green fuels**, or synthetic or electrofuels (e-fuels), are either liquids or in gaseous form which are obtained from renewables using electricity preferably solar or wind.
- **Chemical nature :** Chemically biodiesel is *the methyl esters of long chain carboxylic acids.* Biodiesel is obtained by transesterification of vegetable oil or animal fats with methyl alcohol using sodium metal or sodium methoxide, as catalyst.

Review Questions

Q. 1 What is this branch of "Green Chemistry"?

Q. 2 Explain objectives of green chemistry.

Q. 3 Why is it called as clean chemistry ?

Q. 4 Why is it essential to have green processes ?

Q. 5 List the principles of green chemistry.

Q. 6 Explain the following principles of green chemistry with suitable example :

(i) Prevention of waste
(ii) Maximise Atom economy
(iii) Non-hazardous chemical
(iv) Safer chemical
(v) Auxiliary Substances
(vi) Energy efficiency
(vii) Renewable feedstocks
(viii) Derivatisation
(ix) Catalysts
(x) Degradable products
(xi) New Analytica methods
(xii) Accident prevention

Q. 7 Why is it essential to avoid derivatisation in reaction ?

Q. 8 How maximizing atom economy is beneficial ?

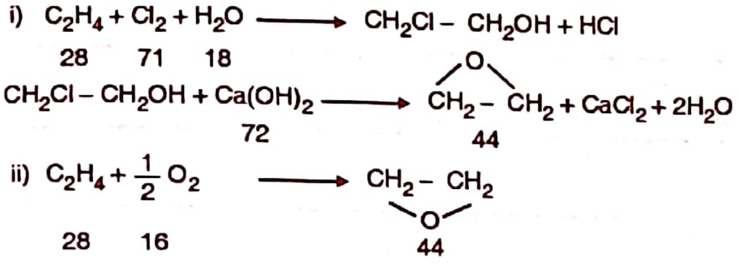
Q. 9 How prevention of waste is advantageous ?

Q. 10 Discuss applications of green chemistry.

Q. 11 Write short note on : SC-CO_2

Q. 12 Calculate % atom economy for following reaction.

(a) Synthesis of ethylene oxide.



i) $\underset{28}{C_2H_4} + \underset{71}{Cl_2} + \underset{18}{H_2O} \longrightarrow CH_2Cl-CH_2OH + HCl$

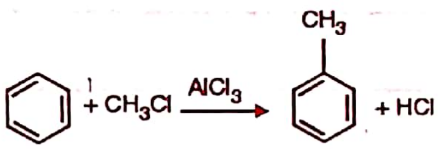
$CH_2Cl-CH_2OH + \underset{72}{Ca(OH)_2} \longrightarrow \underset{44}{CH_2-CH_2}\,(O) + CaCl_2 + 2H_2O$

ii) $\underset{28}{C_2H_4} + \underset{16}{\frac{1}{2}O_2} \longrightarrow \underset{44}{CH_2-CH_2}\,(O)$

[Ans. : (i) 23 % (ii) 100 %]

(b) $CH_3\,CH_2\,CH_2\,Br + KOH \xrightarrow{\text{alcohol}} CH_3\,CH = CH_2 + KBr + H_2O$ [Ans. : 27%]

(c)



[Ans. : 71.5%]

(d) $CH_3CH_2Br + KOH \xrightarrow{H_2O} CH_3CH_2OH + KBr$ [Ans. : 32.6 %]

□□□

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